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PHILIPPINE TERPENES AND ESSENTIAL OILS, I.

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INTRODUCTION.

The Philippines, like all tropical countries, are very rich in plants producing resins, terpenes and essential oils, and this laboratory has been engaged in studying certain of these for the past three years. The identification of the various products from Manila *elemi* and a study of the physical constants of the terpenes derived therefrom have already been reported on by Clover [1] who has also recorded a few notes on resins containing sesquiterpenes.[2] It was shown by Clover that Manila *elemi* on distillation yields 15 to 20 per cent of terpenes, and that by selecting resins from individual trees it was possible to obtain a supply of these in a pure state, those most frequently found being *d*-limonene and *d*-phellandrene. The resin remaining after the terpene is distilled off is a dark, amber colored, semisolid product, readily soluble in organic solvents, and experiments show beyond doubt that it would be a satisfactory raw material for preparing varnishes. The volatile oils derived from Manila *elemi* are valuable for many purposes for which ordinary turpentine is used. However, it was thought that chemical studies on these terpenes might develop more valuable uses to which they could be applied, apart from the large scientific interest which their study possesses; thus a broader applicability of these oils might result and the whole Philippine resin industry be advanced.

[1] *This Journ., Sec. A., Gen. Sci.* (1907), 2, 1.

[2] *Ibid.* 1, 191. A large amount of experimental material has since been accumulated by this Bureau on the subject of some of the native resins.

The terpenes present a difficult field for investigation. The usual methods of organic synthesis often fail in working with them and general methods of passing from one class of compounds to another are not only not well developed, but they frequently fail even with the greatest precautions. The terpenes, being, hydrocyclic bodies, partially unsaturated, are very sensitive to reactions which would present conditions where polymerization is possible, while oxidation and many other reactions often involve their complete destruction or the formation of noncrystalline derivatives and smears. Nevertheless, it appears as if an intimate connection between the terpenes and the essential oils and perfume substances, as well as between them and the plant alkaloids exists structurally, and therefore the investigation of synthetic methods among the terpenes becomes of vital importance. The great need is to discover methods generally applicable of passing smoothly from the terpenes to their derivatives and the means of obtaining the latter in the pure state. The Grignard reaction, which in the last few years has developed so many other fields of organic chemistry, naturally suggests itself, for the hydrogen halides of the terpenes are in almost all cases compounds easily prepared. It was therefore decided in this laboratory to take up the study of the Grignard reaction in its application to the terpene series and although the work is not by any means completed, the results obtained seem to be so promising that it was deemed advisable to publish this preliminary notice so as to reserve the field.

It has definitely been proved that limonene hydrochloride reacts with magnesium in the presence of absolute ether to form a magnesium-halogen compound, and that the latter, when decomposed by water, gives a hydrocarbon $C_{10}H_{18}$, this takes up hydrogen chloride in the cold and, after the action of magnesium and then of water, gives $C_{10}H_{20}$. The reaction of benzaldehyde on the mixed compound of ethyl ether and magnesium hydro-limonene chloride is extraordinary; the carbinol which is to be expected, is not formed, but instead the benzaldehyde behaves as if it contained hydroxyl, decomposing the Grignard body in the same manner as water or an alcohol would. It is at first thought very surprising that benzaldehyde should be capable of reacting as if it possessed a tautomeric form $\begin{matrix} C_6H_5 \\ HO \end{matrix}\!\!>\!C$: However, Freer [3] showed some years ago that aldehydes react with sodium as if they contained hydroxyl groups, and Nef [4] and his students have recently proved that aldehydes, in many cases, do assume the enol form before reacting, so that an equilibrium between enol and keto structure is to be expected in these bodies. It is more difficult to believe in such a structure in the case of benzaldehyde, in which body, if we refer to our ordinary conceptions of organic chemistry, we will need

[3] *Am. Chem. Jour.* (1896), **18**, 552.
[4] *Ann. Chem.* (*Liebig*) (1907), **357**, 258.

to assume that a minute trace of the methylene derivative is always present. However that may be, it is a fact that all substances capable of assuming the enol and keto types respectively act with the Grignard reagent so far as they have been studied, as if composed of the former, thus, acetoacetic ester, urea, thiourea and the amides, etc., all behave toward alkyl magnesium halides as if they contained hydroxyl groups.

EXPERIMENTAL.

The action upon magnesium of limonene hydrochloride dissolved in absolute ether, is not vigorous, or even fairly complete unless certain rigid conditions are met, but if these are adhered to the reaction takes place smoothly and very rapidly to practical completion. Many experiments were undertaken to obtain the best conditions. The limonene hydrochloride must be as pure as possible and in most of my experiments it was twice refractioned *in vacuo;* the ether also must be very pure and absolutely dry. The best results were obtained by the usual procedure of removing all soluble impurities by shaking with small portions of water, then drying the reagent over calcium chloride, distilling from sodium wire and finally keeping the ether over sodium wire in a bottle protected by a tube filled with soda lime. The Grignard body which is produced absorbs oxygen very rapidly, and so in most instances my reactions were conducted in an atmosphere of dry hydrogen. It is desirable to have the magnesium as pure as possible, although satisfactory results may be obtained with magnesium which is not strictly so if it is properly treated beforehand. The persistency with which limonene hydrochloride refuses to react unless all conditions are strictly met is shown by one experiment in which a mixture of limonene hydrochloride, magnesium and ether was placed at ordinary temperature without reaction and finally heated in a sealed tube to 120° to 130° for twenty hours without any change.

The following experiments gave a different result:

Experiment 1.—The limonene was obtained from orange peel oil which was twice refractioned and the terpene then distilled over sodium; its boiling point was 174° to 176° at atmospheric pressure. Specific gravity, $\frac{30°}{4°}=0.8350$; $N\frac{30°}{D}=1.4670$; $A\frac{30°}{D}=110.7$. One hundred and fifty grams of this product were dissolved in an equal volume of dry carbon bisulphide and dry hydrogen chloride was passed for two working days into the liquid, which was kept in a freezing mixture. The product was then washed with water and dilute alkali, dried over calcium chloride, the carbon bisulphide distilled and the product fractioned *in vacuo.* One hundred and ten grams of limonene hydrochloride of a boiling point of 105° to 107° at 20 millimeters were obtained. Specific gravity, $\frac{30°}{4°}=0.9703$; $N\frac{30°}{D}=1.4770$; $A\frac{30°}{D}=73.1°$. The following was the analysis:

	Found (per cent).	Calculated for $C_{10}H_{17}Cl$ (per cent).
Cl	20.1	20.3

The Grignard reaction was conducted in a 400 cubic centimeter bromine flask, in an atmosphere of dry hydrogen. One hundred and fifty cubic centimeters of absolute ether and 7 grams of magnesium filings were placed therein and the reaction was begun with a few drops of ethyl bromide, 45 grams of limonene hydrochloride were then added, whereupon the reaction continued vigorously; after it was completed the product was poured over cracked ice and dilute sulphuric acid carefully added. The ethereal layer was separated, dried over calcium chloride, the ether distilled and the product finally fractioned *in vacuo* with the following results:

Fraction No. 1: B. P. 100° to 102° at 65 millimeters; 25 grams, chlorine free.

Fraction No. 2: B. P. 102° to 110° at 60 millimeters; 5 grams, containing a trace of chlorine.

Fraction No. 3: The residue in the distilling flask, 3 grams, contains a small amount of chlorine.

Fraction No. 1, was redistilled over sodium at ordinary pressure and then yielded 23 grams of an oil boiling between 174° and 176°, with following constants:

Specific gravity, $\frac{30°}{4°}=0.8257$; $N\frac{30°}{D}=1.4585$; $A\frac{30°}{D}=90.3$.

Fractions Nos. 2 and 3 were united and fractioned over sodium, they gave 3 grams of an oil passing over between 180° and 210°, containing no chlorine. The low boiling portion, No. 1, which posseses an ether-like odor, was again distilled at ordinary pressure in an atmosphere of carbon dioxide and 8 grams from the middle portion were taken for analysis. The constants of this fraction were: $N\frac{30°}{D}=1.4565$; the molecular refraction was M=45.5 calculated for $C_{10}H_{18}$ =45.3.

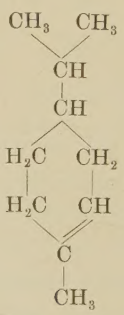
(1) 0.2420 gram substance gave 0.7720 gram CO_2 and 0.2820 gram H_2O.

(2) 0.1621 gram substance gave 0.5160 gram CO_2 and 0.1902 gram H_2O.

	Found (per cent).		Calculated (per cent).	
	(1)	(2)	$C_{10}H_{18}$	$C_{10}H_{16}$
C	86.99	86.85	86.96	88.2
H	12.98	13.07	13.04	11.8

The result leaves little doubt but that the hydrocarbon has the formula $C_{10}H_{18}$, but to assure greater certainty it was decided to convert it into the completely reduced substance, $C_{10}H_{20}$.

This hydrocarbon $C_{10}H_{18}$, is probably the dihydro-limonene:



and identical with the Δ^1 para menthene which Semmler[5] obtained by the

[5] *Ber. d. chem. Ges.* (1903), **36**, 1035.

reduction of limonene hydrochloride with sodium and alcohol at a temperature not higher than 10°. Semmler's dihydro-limonene had a boiling point of 173° to 174°; specific gravity, $20°=0.829$; $N_D=1.463$; Pol.= +40, while the same hydrocarbon prepared from phellandrene hydrochloride by reduction with sodium and amyl alcohol has a boiling point of 171° to 172°; specific gravity, $20°=0.829$; $N_D=1.4601$; Pol.=+25.

Experiment 2.—The limonene was distilled from orange peel oil and had the following constants: Specific gravity, $\frac{30°}{4°}=0.8365$; $A\frac{30°}{D}=117.2$; $N\frac{30°}{D}=1.4680$; the hydrochloride, specific gravity, $\frac{30°}{4°}=0.9675$; $N\frac{30°}{D}=1.4770$; $A\frac{30°}{D}=66.5°$. The analysis gave:

	Found (per cent).	Calculated for $C_{10}H_{17}Cl$ (per cent).
Cl	20.26	20.3

Fifty grams of this substance were now put through the Grignard reaction with 9 grams of magnesium and 150 cubic centimeters of dry ether in the apparatus used for experiment 1, the reaction being started with methyl iodide and iodine. There resulted 38 grams of crude oil (calculated 39.8 grams), containing only 0.61 per cent of chlorine, so that 3 per cent of the total hydrochloride used had not been acted upon by the magnesium. This oil was separated into two fractions by careful distillation *in vacuo* with the following results:

No. 1: B. P. 85° to 86° at 40 millimeters, 29.2 grams containing no chlorine.

No. 2: A residue of 7.3 grams containing chlorine.

Number 1 possessed the peculiar, ether-like odor of the dihydroterpene and gave the following constants: Specific gravity, $\frac{30°}{4°}=0.8258$; $N\frac{30°}{D}=1.4580$; $A\frac{30°}{D}=78.2$. The following was the analysis:

0.1468 gram substance gave 0.4674 gram CO_2 and 0.1725 gram H_2O.

	Found (per cent).	Calculated for $C_{10}H_{18}$ (per cent).
C	86.81	86.96
H	13.09	13.04

Twenty-eight grams of the oil $C_{10}H_{18}$ were now diluted with an equal volume of carbon bisulphide, dry hydrogen chloride passed into the mixture to saturation and the whole kept in ice and salt for ten hours. The product was purified in the usual manner and yielded 23 grams of an oil boiling between 110° and 115° at 30 millimeters pressure, 8 grams of residue remaining in the distilling flask. The following were the constants: Specific gravity, $\frac{30°}{4°}=0.931$; $N\frac{30°}{D}=1.4624$; $A\frac{30°}{D}=6.8°$. The analysis gave:

	Found (per cent).	Calculated for $C_{10}H_{19}Cl$ (per cent).
Cl	20.4	20.3

A gram of this oil when treated with sodium ethylate in alcohol, yielded a liquid of very pleasant odor, probably the corresponding ethoxy-derivative. Twenty grams of the chloride so produced were subjected to the Grignard reaction in an atmosphere of hydrogen, 4 grams of magnesium and 60 cubic centimeters of ether being used, the reaction being inaugurated with a little methyl iodide, it proceeded vigorously. There were obtained 14 grams of a chlorine-free oil

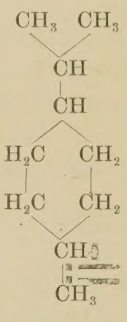
boiling between 80° and 83° at 40 millimeters pressure. It was redistilled over sodium at ordinary pressure, the final yield being 12 grams of oil of a boiling point 171° to 174°. The product is colorless, with an ethereal odor somewhat resembling that of benzene. Specific gravity, $\frac{30°}{4°}=0.8052$, $N\frac{30°}{D}=1.4459$, $A\frac{30°}{D}=3.7$. The analysis gave the following results:

0.2037 gram substance gave 0.6397 gram CO_2 and 0.2602 gram H_2O.

	Found (per cent).	Calculated for $C_{10}H_{20}$ (per cent).
C	85.64	85.72
H	14.31	14.28

This oil, $C_{10}H_{20}$, dissolves slowly in concentrated sulphuric acid (specific gravity 1.84) without warming or the evolution of sulphur dioxide, giving a slightly reddish solution. The oil is recovered unchanged if the solution is quickly treated with water, more prolonged action of sulphuric acid gives higher boiling products containing sulphur. Concentrated sulphuric acid acts violently on limonene as well as on its reduction product $C_{10}H_{18}$, with marked resin formation and the evolution of sulphur dioxide. Bromine reacts with $C_{10}H_{20}$ by substitution, with the evolution of hydrogen bromide.

Sabatier and Senderson[6] reduced limonene with hydrogen in the presence of nickel sponge at 250° and thus obtained tetrahydro-limonene, the *p*-methylisopropyl-cyclohexane, $C_{10}H_{20}$.



This substance has a boiling point of 169° to 170° and a specific gravity at $\frac{0°}{4°}$ of 0.8132. However, this hydrocarbon was probably not pure, as the authors state, "accompagné d'une petite quantite des produits de deboublemént et para diméthyl et para méthyl éthyl cyclo hexane." Renard[7] obtained from resin oil a hexahydrocymol boiling between 171° and 173° and having a specific gravity of 0.8116 at 17°.

No doubt exists from the above experiments but that I have successively passed from $C_{10}H_{16}$ through $C_{10}H_{18}$ to $C_{10}H_{20}$. An easy method of obtaining tetra and hexahydrobenzene derivatives from terpenes and their derivatives is therefore at hand. It might be questioned that a compound of limonene hydrochloride with magnesium, obtained after the

[6] *Compt. rend. Acad. d. sc.* Par. (1901), **132**, 1256.
[7] *Ann. Chim. Phys.* (1884), (6) **1**, 230.

usual manner of the Grignard reaction, is really produced in this instance, as reactions undertaken to produce the classes of synthetic products usually formed by working with similar magnesium derivatives of other halides have not been successful, but the following quantitative experiments remove all doubt of the existence of such a body.

Experiment 3.—Ten grams of limonene hydrochloride were subjected to the action of magnesium after the usual method of Grignard. The ether, containing the soluble magnesium addition product was then filtered in an atmosphere of dry hydrogen in a similar apparatus to that employed by Freer [8] in his work on sodium acetone. The filtrate was decomposed by means of cracked ice and dilute acid in the usual manner and the magnesium contained in an aliquot portion of the aqueous solution then determined.

	Found (per cent).	Calculated for $C_{10}H_{18}MgCl$ (per cent).
Mg	12.4	12.2

It will be noted that a slight excess of magnesium was found and it seems probable that this is due to the few drops of methyl iodide which must be added to start the reaction. The ethereal solution after adding the ice and acidifying gave 5.7 grams of $C_{10}H_{18}$, with the usual properties. Another fact to be remembered in considering the formation of the magnesium addition product is that there is always a considerable evolution of heat when the latter is decomposed by water, a fact which is difficult to explain if it is assumed that the magnesium has simply acted on limonene hydrochloride as a reducing agent.

It is not advisable at the present time to discuss at greater length which of the possible bodies of the empiric formula $C_{10}H_{18}$ is formed during this reaction. The second reduction product of the formula $C_{10}H_{20}$ always, so far, has possessed a slight optical rotation and this fact renders it probable that the latter has not been obtained entirely pure. However, the above experiments prove beyond any doubt that limonene hydrochloride reacts with magnesium after the normal manner of the Grignard reaction.

It has been shown that alcohol or other compounds containing hydroxyl react with the products of the Grignard reaction according to the following scheme:

$$ROH + R'MgX = ROMgX + R'H.$$

The reactions with water which have been outlined gave this result. The next step was to study the action of aldehydes upon the product of the interaction of magnesium and limonene hydrochloride in the presence of absolute ether, and benzaldehyde was the first representative of the class selected.

Experiment 4.—Forty grams of limonene hydrochloride, 10 grams of magnesium and 150 cubic centimeters of absolute ether were allowed to react in an atmosphere

[8] *Ann. Chem.* (*Liebig*), (1894), **278**, 123; **283**, 38.

of dry hydrogen in a strong flask fitted with a mechanical stirrer. After the change was complete, 30 grams of benzaldehyde, dissolved in an equal volume of absolute ether, were added, drop by drop. The reaction was violent, taking place with a considerable evolution of heat, while at the same time a nearly solid, yellowish-colored substance separated. The product was now vigorously stirred for one hour, it was then treated in the usual manner, the ethereal layer being well shaken out with acids and alkalies. The alkaline solution on acidifying gave 2.3 grams of benzoic acid. As the neutral solution, after distilling the ether, did not readily solidify, it was fractioned *in vacuo* with the following result:

No. 1: B. P. 85° to 90° at 30 millimeters, 38 grams;

No. 2: B. P. 90° to 130° at 20 millimeters, 3 grams;

No. 3: B. P. 130° to 180° at 20 millimeters, 7 grams;

Tar-like residue, 4 grams.

Decomposition appeared to take place above 130° and excepting the first fraction, there was no indication of a constant boiling substance. No solid bodies could be obtained from numbers 2, 3 and 4, in ice and salt.

Fraction number 1 was dissolved in low boiling petroleum ether and treated with an excess of phenylhydrazine.[9] Thirty-five grams of benzaldehyde phenylhydrazone of a melting point of 154° were thus separated, this quantity corresponds to 18.9 grams of benzaldehyde. The remainder of fraction number 1 consisted for the greater part of $C_{10}H_{18}$.

The higher boiling fractions proved themselves to be an inseparable mixture containing much tar.

As the principal products of the reaction were benzaldehyde and $C_{10}H_{18}$, it was thought possible that the benzaldehyde had not acted upon the Grignard addition product at all, but on the contrary that the yellowish, nearly solid substance was produced by the action of benzaldehyde on magnesium powder in a manner similar to the substances formed by the interaction of sodium and benzaldehyde, as noted by Beckmann and Paul.[10]

To disprove this assumption the action of benzaldehyde on magnesium was studied.

Experiment 5.—Five grams of magnesium powder in absolute ether were rendered active by means of iodine, and a solution of 10 grams benzaldehyde in absolute ether was then added. No action took place even after the whole was heated on a reflux condenser for one hour.

The following experiment demonstrates that when benzaldehyde acts on the product formed by the action of magnesium on limonene hydrochloride it does so in such a manner as *at once to liberate* $C_{10}H_{18}$, or in other words, just as if benzaldehyde were an *alcohol* in this instance.

Experiment 6.—Forty grams of limonene hydrochloride, 10 grams of magnesium and 150 cubic centimeters of absolute ether were taken. The apparatus was in principle like that employed by Freer in his work on sodium acetone. A strong,

[9] It has been shown in this laboratory that benzaldehyde can promptly and satisfactorily be separated from its solution in petroleum ether by phenylhydrazine.

[10] *Ann. Chem.* (*Liebig*), (1891), **266**, 6.

wide-mouthed flask was fitted with a stopper with five holes, the latter carrying respectively: (1) The inlet for dry hydrogen; (2) the stirrer set in a mercury trap, (3) a dropping funnel, (4) the reflux condenser which was fitted with a glass stopcock sealed into it, and which was protected at its upper end by a tube of soda-lime and (5) a tube running to the bottom of the reaction flask. The latter had sealed onto it a funnel fitted with an asbestos filter and was connected with a filter flask by means of a tube and glass stopcock. The filter flask could be evacuated in the usual manner. After the reaction according to Grignard was complete, 25 grams of benzaldehyde dissolved in absolute ether, were slowly dropped into the flask. The usual, violent reaction with much evolution of heat took place and the yellowish, semisolid substance separated, the whole soon becoming so thick that it was impossible to run the stirrer. After one-half hour, absolute ether to dilute was added in small portions, and by closing the reflux and opening the filter funnel connected with a slight vacuum, the reaction product was separated into two portions, one soluble and the other insoluble in absolute ether; of course, care was taken thoroughly to wash the insoluble part with absolute ether. Both the soluble and insoluble portions were now decomposed by means of ice and acid in the usual manner, the etheral solutions resulting were separated, dried and the ether distilled.

Soluble portion: The aqueous solution obtained by decomposing the soluble portion contains *no magnesium*. The neutral oil when treated with an excess of phenylhydrazine in petroleum ether gave 4.1 grams of benzaldehyde phenylhydrazone of a melting point of 153°. The excess of phenylhydrazine was removed by means of dilute sulphuric acid, the petroleum ether distilled and the product fractioned *in vacuo*. Twenty-five grams of an oil boiling between 90° and 93° at 50 millimeters pressure was thus obtained. This fraction contained no chlorine, and after two distillations over sodium at ordinary pressure had the following properties: Boiling point, 175° to 177°, thermometer wholly in the vapor; specific gravity, $\frac{30°}{4°}=0.8250$; $N\frac{30°}{D}=1.4605$; $A\frac{30°}{D}=72.7°$. These properties demonstrate it to be the same compound $C_{10}H_{18}$, produced by the action of water on the body formed by magnesium and limonene hydrochloride. The residual 7 grams in the distilling flask contained a little chlorine and seemed to consist of the diterpene always obtained as a part of the product of the action of magnesium on limonene hydrochloride.

Insoluble portion: Thirty-four grams of benzaldehyde phenylhydrazone of a melting point of 154° after one crystallization from ligroin were obtained by the usual methods from this part.

There remained 6.6 grams of a tar-like oil after removing the excess of phenylhydrazine and from this neither a crystalline solid nor a constant boiling substance could be separated.

Experiments 1, 2, and 3 clearly demonstrate that limonene hydrochloride forms a compound with magnesium of the usual nature of the Grignard addition products, the body being soluble in ether and carrying the theoretical amount of magnesium. Experiment 6 proves that benzaldehyde, acting on this substance, forms a solid body carrying all the magnesium and that this solid when decomposed with water, principally gives benzaldehyde, at the same time the product *soluble in ether and free from magnesium* contains the dihydroterpene $C_{10}H_{18}$, which has been split off from the Grignard body just as if water had reacted with

this product. Thus the principal reaction of benzaldehyde on dihydro-limonene magnesium chloride would seem to be:

$$C_{10}H_{17}MgCl + C_6H_5CHO = \underset{\text{(Insoluble in ether.)}}{C_6H_5COMgCl} + \underset{\text{(Soluble in ether.)}}{C_{10}H_{18}}.$$

The evidence for this assumption is made stronger by the following experiments:

Experiment 7.—The following quantities were taken: Limonene hydrochloride, 35 grams; specific gravity, $\frac{30°}{4°}=0.9770$; $A\frac{30°}{D}=54.6°$; $N\frac{30°}{D}=1.4768$; magnesium powder, 6 grams; absolute ether, 100 cubic centimeters. The reaction was carried on throughout as in experiment 6, 23 grams of benzaldehyde free from benzoic acid being used.

Soluble portion: This portion contained no magnesium. The total oil was 20.2 grams, from which, distilled *in vacuo*, the following fractions were obtained:

No. 1: B. P. 75° to 78° at 25 millimeters, 17.2 grams.

No. 2: Residue 2.6 grams.

The usual means of separation gave 4.5 grams of benzaldehyde phenylhydrazone melting at 155° and 156°. The remaining oil, after the removal of the phenylhydrazine, had the following properties: Boiling point, 174° to 176°; specific gravity, $\frac{30°}{4°}=0.8248$; $N\frac{30°}{D}=1.4590$; $A\frac{30°}{D}=37°$; it was therefore $C_{10}H_{18}$.

Summary of the soluble portion.—Benzaldehyde 2.3 grams; $C_{10}H_{18}$, 14.7 grams; residue (diterpenes, etc.), 2.5 grams.

Insoluble portion: The total oil was 31 grams, containing a trace of chlorine. The product, distilled *in vacuo*, at 40 millimeters gave the following fractions:

No. 1: B. P. 80° to 85° at 15 millimeters, 18 grams.

No. 2: B. P. 85° to 215° at 15 millimeters, 7 grams.

No. 3: 3.5 grams of residue.

There were obtained from the above, 22.8 grams of benzaldehyde phenylhydrazone melting at 156° and a liquid with the constants: Boiling point, 175° to 176°; specific gravity, $\frac{30°}{4°}=0.8254$; $N\frac{30°}{D}=1.4590$; $A\frac{30°}{D}=36.8$. There was also isolated 1.1 gram of benzoic acid.

Summary of the insoluble portion.—Benzaldehyde, 12.3 grams; $C_{10}H_{18}$, 7 grams; benzoic acid 1.1 gram, and 8.5 grams of inseparable, high boiling compounds. The presence of the dihydro-limonene is probably due to imperfect washing of the insoluble solid by the ether. This is readily understood when the sticky nature of this body is considered.

Experiment 8.—This experiment was not performed in the elaborate apparatus we had constructed, but instead was carried out in a bromine flask in an atmosphere of dry hydrogen on a water bath.

The following quantities were taken: Limonene hydrochloride, 35 grams; magnesium powder, 6 grams. After the magnesium addition product had been formed, 23 grams of benzaldehyde were added. The usual violent reaction accompanied by the separation of the yellowish solid took place, the whole being finally heated with steam for fourteen hours, during which time the ether rapidly evaporated, as an ordinary reflux condenser does not hold that solvent in this climate. The

product was covered with fresh ether, decomposed with ice and dilute acid in the usual manner and the solvent distilled, 55 grams of an oil, which was fractioned *in vacuo*, being obtained.

No. 1: B. P. 70° to 100° at 15 millimeters, 28 grams.

No. 2: B. P. 100° to 150° at 15 millimeters, 12 grams.

No. 3: B. P. 180° to 210° at 15 millimeters (metal bath to 280°), 8 grams.

No. 4: Tarry residue, 4.5 grams.

Number 1 gave 14 grams of benzaldehyde phenylhydrazone and 19 grams of $C_{10}H_{18}$, specific gravity, $\frac{30°}{4°}=0.8304$; $N\frac{30°}{D}=1.4640$. Five grams of benzoin melting at 137° after recrystallization from ligroin and 1.2 grams of benzoic acid melting at 121° were obtained from Numbers 2 and 3. The residual 14 grams was a tar-like oil, which regenerated considerable quantities of benzaldehyde on being boiled with dilute acids. It is probably in greater part a mixture of polymers of benzaldehyde.

It is seen from the above that *benzoin*, which should be expected in quantity in the residues of all of these reactions, as it should be formed from a benzaldehyde magnesium compound, is really produced if this compound is heated.

Experiment 9.—There were used 50 grams of limonene hydrochloride and 10 grams magnesium, the reaction (which in this instance unfortunately did not reach completion) being conducted in the apparatus with a filter tube described in Experiment 6. A small amount of the ethereal solution was filtered, decomposed with ice and acid and analyzed, giving 2.6 grams of organic liquid, principally $C_{10}H_{18}$, and 0.307 gram magnesium (calculated Mg=12.2, found=10.3 per cent). The remainder was now also filtered from the unchanged magnesium and from the insoluble portion of the ethereal compound of hydro-limonene magnesium chloride, and the filtrate, which now only contained the *soluble* portion of the addition product, was then treated with 35 grams of benzaldehyde. The usual evolution of heat took place and the yellow solid already described separated, so that the magnesium addition product produced according to the method of Grignard and separated from all other substances by filtration, is in reality the compound taking part in the reaction, any excess of benzaldehyde, or of magnesium powder, which is generally present, not taking part therein. The yellow solid produced from this soluble portion was now again filtered in an atmosphere of dry hydrogen and well washed with absolute ether; it was finally transferred to another flask and placed under absolute ether, it is designated below as the *insoluble portion*. The united etherial solution filtered from this insoluble substance, and the ether used to wash it are termed the *soluble portion*.

The soluble portion: This part was *free from magnesium* and after removing the ether it consisted of an oil which weighed 45 grams in the crude state and which gave the following fractions when distilled *in vacuo:*

No. 1: B. P. 80° to 90° at 20 millimeters, 33 grams.

No. 2: B. P. 90° to 110° at 20 millimeters, 5 grams.

No. 3: A residue of tar, 6 grams.

The above fractions, when treated with the usual reagent gave 35 grams of benzaldehyde phenylhydrazone melting at 155°, representing the excess of benzaldehyde added to the above solution and 14.8 grams of $C_{10}H_{18}$ of a specific gravity at $\frac{30°}{4°}$ of 0.8262 and a refractive index, $N\frac{30}{D}$ of 1.4584, the remainder consisted of unchanged limonene hydrochloride and of diterpenes.

The insoluble portion: One and four-tenths grams of the solid remaining under ether was removed, washed with absolute ether, dried rapidly on a porous plate, weighed to a tenth of a gram and thrown into water. The substance proved to be exceedingly unstable in the air, the yellow powder soon becoming very hot, with the separation of a red oil, a behavior similar to that of sodium acetone, while at the same time a very marked odor of benzaldehyde is developed. The powder dissolved rather slowly when thrown into water so that it was necessary to add a little dilute sulphuric acid. The aqueous solution was extracted twice with small quantities of ether, the solvent allowed to evaporate slowly in the air and a crystalline body, which melted at 121° and which proved to be benzoic acid was separated. A very small amount of an oily residue, having the odor of benzaldehyde remained. Magnesium and chlorine determinations were made on aliquot portions of the aqueous solution with the following result:

		Calculated (per cent) for	
	Found (per cent).	$C_6H_5COMgCl$	$C_6H_5C<\begin{matrix}H\\OMgCl\\C_{10}H_{17}\end{matrix}$
Cl	20.71	21.5	11.2
Mg	12.8	14.7	7.9

These figures, considering the method used and the difficulty of washing out all free benzaldehyde and the certainty of some oxidation during the transfer, agree very well with those calculated.

The remainder of the solid was heated for three hours on a reflux condenser with 18 grams of benzoyl chloride. The product was then treated with alkali and the neutral part, on distillation, gave 4 grams of benzaldehyde, 1 gram of a solid, mostly benzoic acid[11] and 5 grams of tarry residue. From the alkali 25 grams of benzoic acid were recovered, it is therefore evident that the solid addition product does not react with benzoyl chloride.

Experiment 10.—There were used 10 grams of limonene hydrochloride, 3 grams of magnesium and 40 cubic centimeters of absolute ether. The apparatus was arranged as follows: Flask No. 1 in which the Grignard reaction took place, was fitted with a reflux condenser and a filter tube running to flask No. 2; in this second flask, which also carried a reflux condenser, the filtrate from No. 1 was treated with benzaldehyde, and a second filter tube delivered the filtrate from No. 2 after this reaction, into flask No. 3. All parts were arranged so that they could constantly be kept filled with dry hydrogen. After the Grignard reaction was completed in No. 1, the filtrate which was passed over into No. 2 was treated with benzaldehyde and the solid substance which was formed was well washed with absolute ether, all soluble portions and washings being sucked over into No. 3. On final analysis No. 3 was found to contain no magnesium and only $C_{10}H_{18}$, and the excess of benzaldehyde. The solid in No. 2 was placed under benzene (dried by distilling over sodium wire) and dry oxygen was run into it for eight hours. The reaction is not very marked, this result possibly being due to the fact that the solid forms dense cakes, difficult to penetrate. However, a gradual reddening took place so that the whole, when the current of oxygen was finally shut off had assumed a deep red color. There resulted 1.4 grams of benzoic acid melting at 121°; 0.9 grams benzaldehyde proved by transference into the phenylhydrazone melting at 155° and 1.2 grams of tar. Magnesium and chlorine determinations were made and when calculated on the total substance finally obtained, gave the numbers 11.8 per cent for magnesium and 20.4 per cent for chlorine. Calculated for $C_6H_5COMgCl$, magnesium 14.7 chlorine 21.5 per cent.

[11] Benzaldehyde oxidizes very rapidly in this hot, moist climate.

Experiment 11.—There were employeed 20 grams of limonene hydrochloride, 100 cubic centimeters of absolute ether and 10 grams of magnesium prepared with iodine according to the method of Von Baeyer.[12] This means of rendering the magnesium active was finally found to be the most satisfactory, as with the metal so prepared the Grignard reaction starts immediately without the aid of any other catalyzer and continues to completion with great vigour. The reaction was carried out in the apparatus used for Experiment 10, 24 grams of benzaldehyde (free from benzoic acid) being added to flask No. 2. The contents of all flasks were worked up in the usual manner.

Flask No. 1 gave 5.2 grams of an oil, principally $C_{10}H_{18}$, representing the portion of $C_{10}H_{17}MgCl$ which was insoluble in the quantity of absolute ether used. The precipitate with benzaldehyde formed in flask No. 2 was very thoroughly washed with absolute ether and immediately worked up; the total oil being 10.6 grams. The following analytical data were obtained:

15.56 grams substance (calculated) gave 1.93 grams magnesium and 3.03 grams chlorine.

	Found (per cent).	Calculated (per cent).
Mg	12.4	14.7
Cl	19.48	21.5

From the 10.6 grams of total oil there were isolated 0.2 gram benzoic acid, 9.1 grams of an oil boiling between 177° and 182°, the latter was converted into 16.5 grams benzaldehyde phenylhydrazone melting at 154°, and 1 gram of a tarry residue remained in the distilling flask.

Flask No. 3 contained only a trace of magnesium and yielded a total of 21 grams of oil boiling between 170° and 183°; from the latter a quantity of benzaldehyde phenyldrazone corresponding to 12.96 grams benzaldehyde was isolated. The remaining liquid which in amount was 10.8 grams, after removing the excess of phenylhydrazine, was the dihydro-terpene $C_{10}H_{18}$. The calculated amount of pure $C_{10}H_{18}$ which would be set free from $C_{10}H_{17}MgCl$ by 9 grams of benzaldehyde (formed by decomposing this magnesium compound in flask No. 2) is 12.4 grams, if the course of the reaction is that which has been assumed in this paper. This agreement is a close one when the inevitable losses in fractionation are considered. In this experiment, therefore, the reaction has been shown to proceed *quantitatively* according to our assumptions.

The combination of magnesium chloride and benzaldehyde which has been so fully discussed, when freshly prepared is exceedingly unstable in the air, oxidizing upon exposure with a marked evolution of heat and with reddening. When left standing under absolute ether it is fairly stable, especially if present in a thick layer, so that if such a thick layer is allowed to stand over night in the open air but little benzoic acid is obtained, the benzaldehyde on acidifying being in greater part recovered as such. Oxidation is rapid if the solid is suspended in ether and a stream of air or of oxygen is passed in, but under these circumstances peroxide formation takes place, and for this reason benzene was chosen instead of ether.

It is entirely premature at the present time to enter into a discussion of

[12] *Ber. d. Chem. Ges.* (1905), **38**, 2759.

the constitution of this addition product. The simplest assumption would assign to it a formula $C_6H_5COMgCl$. The structure $\begin{matrix} C_6H_5C{-}O{-}MgCl \\ \| \\ C_6H_5C{-}O{-}MgCl \end{matrix}$ does not seem probable, for neither benzoin nor benzil could be found among the substances obtained by decomposing the compound with water, excepting in one experiment (number 8) where heat was used for a long time and where this result was to be expected. However, it is certain that when benzaldehyde acts on the etherial compound of hydrolimonene magnesium chloride, the former reacts as it would do if it contained a hydroxyl group. As in this instance benzaldehyde reacts as if it were an alcohol, it is not surprising to find that acetone does the same, as acetone often assumes the enol form during reactions as, for instance in the production of sodium acetone and during its condensations, many of which are best explainable on the assumption of a compound of the structure $CH_3 . COH : CH_2$. It was nevertheless deemed advisable to undertake an experiment with acetone as the reagent.

Experiment 12.—There were used limonene hydrochloride, 35 grams; magnesium, 10 grams, and absolute ether, 100 cubic centimeters. The Grignard reaction was allowed to take place in a bromine flask, after it was complete, 13 grams of carefully purified and dried acetone were slowly added. A considerable evolution of heat, as is the case with benzaldehyde, was observed and the separation of a solid which at first was red, then yellow and finally white took place. After the reaction has ceased, the product was treated as was the case when benzaldehyde was the reagent. The neutral oils were distilled *in vacuo* and gave the following fractions:

No. 1: B. P. 73° to 80° at 15 millimeters, 20 grams.

No. 2: B. P. 80° to 110° at 15 millimeters, 7 grams.

No. 3: Residue, 2 grams.

Number 1 was identified as $C_{10}H_{18}$ as it had the following constants: Boiling point, 174° to 176°; specific gravity, $\frac{30°}{4°}=0.8280$; $N\frac{30°}{D}=1.4630$.

Number 2 contained a considerable amount of chlorine and the oil was doubtless a mixture of unchanged limonene hydrochloride and diterpenes. The method of Deniges[13] showed 12.6 grams of acetone to be present in the aqueous solution.

This result is parallel with the one obtained with benzaldehyde and therefore, in this reaction, also, acetone assumes the rôle of propen–1–ol–2.

These experiences with limonene hydrochloride were of sufficient interest to warrant a study of the action of benzaldehyde on other magnesium organic halides, for it might be true that in each instance a certain proportion of the reduced hydrocarbon might be produced, owing to the small percentage of the enol form present in the aldehyde; with this end in view a study of the reaction between benzyl magnesium chloride

[13] *Compt. rend. d. Acad. sci.* Par. (1898), **127**, 963; *Ann. Chim. Phys.* (1899), (6), **18**, 400. *Bull Soc. Chim.* (1899), (3) **21**, 241.

and benzaldehyde was undertaken. Thus Grignard[14] states that benzyl magnesium halides do not react in the normal manner with aldehydes, the principal product of the reaction being dibenzyl, and Hell[15] and his students, depending upon the conditions, obtained both the carbinol and stilben in this reaction.

Several experiments under varying conditions were performed and phenyl-benzyl carbinol was always obtained in large quantities, but in no case could toluol be detected. Phenyl-benzyl carbinol is readily obtained in the pure state by distillation of the reaction product *in vacuo*. It boils from 167° to 170° at 10 millimeters pressure and immediately solidifies in the receiver, the room temperature being 30° to 33°. Hell speaks of the difficulty he experienced in obtaining the carbinol in a solid form when working in the summer. Crystallized twice from ligroin (in which solvent when it is boiling it is quite soluble, whereas it is almost insoluble in the cold), it melts at 67° to 68°. The melting points given for phenyl-benzyl carbinol in the older literature are too low.[16]

With concentrated sulphuric acid it gives a white tar, just as benzhydrol gives a red tar with the same reagent.

As the method of preparing benzhydrol[17] in quantity has in the past been tedious to apply, and as the Grignard reaction was under consideration, it was decided to ascertain if it might be available for this purpose. Using chlor- or brom-benzol, magnesium and ether, and treating the reaction product with benzaldehyde, the results leave nothing to be desired as to yield, ease of manipulation and time consumed, so that this method will undoubtedly replace the longer ones formerly used in preparing this compound.

SUMMARY.

Limonene hydrochloride reacts with magnesium to form a hydrolimonene magnesium chloride, soluble in absolute ether, the union taking place normally according to the type of reactions discovered by Grignard. This addition product when decomposed by water gives a dihydro-terpene $C_{10}H_{18}$.

A method is developed by means of the Grignard reaction of passing from terpenes and their derivatives to di- and tetrahydro-terpenes and

[14] *Ann. de l'Université de Lyon* (1901), N. S. **6**, 1–116; *Chem. Centrbl.* (1901), **II**, 623.

[15] *Ber. d. Chem. Ges.* (1904), **37**, 453, 225, 1429.

[16] Limpricht and Schwanert: *Ann. chem.* (*Liebig*), (1870), **155**, 62. Goldberg: *Ibid.* (1874), **174**, 332. Knovenagel and Arndts: *Ber. d. chem. Ges.* (1902), **35**, 1987. Sudborough: *J. chem. Soc.* London (1895), **67**, 605. Beilstein II, 1079 gives M. P. 42° probably a misprint for 62°. The error has been copied into Richter's Lexikon der Kohlenstoffverbindungen.

[17] Nef: *Ann. Chem.* (*Liebig*), (1897), **298**, 202. Bacon: *Am. Chem. Jour.* (1905), **33**, 68.

their derivatives, and thus a very simple and accessible means of preparing tetra- and hexahydro-benzene derivatives is at hand.

It has been proved by quantitative experiments that with hydro-limonene magnesium chloride, benzaldehyde acts as if it contained a hydroxyl group.

The solid product of the action of benzaldehyde upon hydro-limonene magnesium chloride gives analytical data which point to the formula $C_6H_5COMgCl$. When decomposed with dilute acids this compound regenerates nearly quantitative amounts of benzaldehyde, and only when it had been heated for a long time are products like benzoin obtained, which would indicate a double molecule.

The compound $C_6H_5COMgCl$ is, when freshly prepared, very unstable in the air, its behavior being much like that of sodium acetone. Acetone, like benzaldehyde, also reacts as if it contained a hydroxyl group.

No analogous reaction was obtained from benzyl magnesium chloride and benzaldehyde.

Work with the Grignard reaction in the field of the terpenes will be continued.

PHILIPPINE TERPENES AND ESSENTIAL OILS, II. YLANG-YLANG OIL.

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INTRODUCTION.

The ylang-ylang oil industry is the most important and in fact at present practically the only perfume-oil industry in the Philippines. Like Manila hemp, the ylang-ylang (flower of flowers) is peculiarly a product of the Philippines, as the oil distilled in other tropical countries, prepared from the same tree, is not ranked in the same class, as regards quality, with the product of this Archipelago, but is sold as "cananga" oil. Ylang-ylang oil is obtained by steam distillation from the flowers of *Canangium odoratum* Baill. (*Cananga odorata* Hook. f. et Th.). Some idea of the magnitude of the industry may be obtained from the following extracts from the reports of the Philippine custom-house showing the amounts of this oil exported during the fiscal years named:

Table I.—*Export of ylang-ylang oil from 1900 to 1907, inclusive.*[1]

Year.	Kilos.	Year.	Kilos.
1900	19,647	1904	10,917
1901	7,515	1905	13,395
1902	11,847	1906	27,909
1903	17,826	1907	27,036

Figures available for the Spanish régime.

Year.	Kilos.	Year.	Kilos.
1885	1,703	1890	1,612
1886	1,487	1892	11,095
1887	1,181	1893	2,284
1888	.899	1894	1,621
1889	1,080		

[1] These figures represent gross weights of the packages and hence do not represent the actual amounts of oil exported, on which no figures are available. To obtain the actual weights of ylang-ylang oil exported the figures given should probably be divided by ten.

It is thus evident that the industry is rapidly increasing in magnitude, as perfumers are now using this fine oil in an increasing number of products. As the industry is peculiarly one belonging to the Philippines, this laboratory has undertaken studies on the oil and the best means of its distillation, with the view of improving the methods of manufacture and of the quality of the oil. The results thus far obtained are recorded in this paper.

GENERAL TRADE CONDITIONS.

The general trade conditions in the ylang-ylang oil industry are not particularly promising for a person with limited capital who desires to engage in this business. Necessarily, the price of the oil depends upon its quality, but the establishment of a brand is of very great importance. Oils of long established brand command a higher price than unbranded ones, or than oils of newer brands, although the latter may be fully as good in every respect. Many European houses buy only through Manila firms with whom they have contracts and will not purchase oil from others, no matter what the quality may be. Nevertheless, there is a large open market, especially with French houses, for *first-class* oils, and oils of the very best quality can always be sold. The price naturally varies according to the supply and demand, but the very best oils may be counted upon to bring about 200 pesos, Philippine currency, per kilo [2] and those of established brands bring even higher prices. The conditions in regard to second-grade oils are not by any means as favorable.[3] The demand for these oils is small, probably because of competition with cananga oil and with artificial ylang-ylang oil. Most of the Manila distillers manufacture both first and second grade oils and because of their trade connections they are usually able to dispose of stocks of the latter. The distillers in the provinces who, because of ignorance of the best methods of distillation and of poor apparatus, usually manufacture only second-grade oils, often find great difficulty in selling their product. These provincial distillers are generally anxious to realize quickly on their stocks, which they sell to the Manila firms for the best price offered. The price paid in Manila for such provincial oils is about 30 to 70 pesos, Philippine currency, per kilo. There is often so little demand for second quality oils that they can not be sold in Manila for any price, and the European market for this grade is frequently so inactive that distillers may have such oils on their hands for as long a period as two years before disposing of them.

[2] One peso, Philippine currency, is equal to one-half a dollar, United States currency.

[3] Interesting in connection with the present prices of ylang-ylang oil is Gals article on this substance (*Compt. rend. acad. d. Sc. Par.* (1873), **76**, 1482, in which it is stated that the price of the oil at that time was 2,500 francs the kilo. He calls the oil essence of alan-gilan or hilan-hilan from *Unona odoratissima*, a synonym of *Canangium odoratum*.

In general, the distillers do not own their own groves of ylang-ylang trees, and the market for the flowers in the region around Manila is in a very unsatisfactory condition for the distiller. The large number of distilleries in Manila causes keen competition for the flowers; as a result the quality sold is very poor and the price is high. One of the largest firms in this business states that the flowers are of a much poorer grade during the past few years than they were several years ago.

The flowers are usually picked in the night and are collected in small lots early in the morning by native brokers who deliver them at the distilleries. The natives make a practice of wetting the flowers with as much water as they will absorb and there will often be leaves, twigs, and other substances mixed in with them to add weight. The distillers hardly dare refuse such materials, although the quality is poor, for fear their supply may be altogether cut off. I should estimate that over three-fourths of the flowers brought to the distillers in Manila are unripe and green, although the ripe, yellow product gives a larger yield of much superior oil. The price of flowers in Manila varies from 20 to 40 centavos, Philippine currency, per kilo, the average probably being as high as 30 centavos.[4] Many people in the Islands have an idea that the ylang-ylang distillers make a tremendous profit. From my observation, of the business I can not believe this opinion to be well founded. It probably requires on an average 350 kilos of flowers to produce 1 kilo of first-class oil and this amount will also probably give an additional three-quarters of a kilo of second-class oil. Thus the flowers for 1 kilo of first-class oil will probably cost 115 pesos, Philippine currency, and after the cost of steam and water used, of skilled supervision, interest and depreciation of the plant are added only a legitimate profit is left. The grower seems to be the one who makes the large profits in this industry, as I have heard of trees being sublet by the year for 2 pesos per month, the renter expecting to make a profit from the flowers which he can pick from the tree. This would mean a production of at least 80 kilos of flowers from one tree during a year. We have no figures, nor have we been able to obtain any reliable data on the point of the yield of flowers from one tree, but there is no doubt but that large trees bear very luxuriantly. In Manila, the best flowers are usually obtained in May and June, but the season just passed

[4] In Piesse's Art of Perfumery, London, (1891), 134, is found an interesting error in the statement that ylang-ylang flowers are adulterated with flowers of champaca (*Michelia champaca* Linn.) to cheapen the quality of the oil. As a matter of fact champaca flowers sell in Manila for as high as 1 peso, Philippine currency, per kilo with a good demand as compared to ylang-ylang flowers at about 30 centavos, Philippine currency, per kilo, and oil of champaca is much more expensive than oil of ylang-ylang. An idea prevails in Manila that the distillers make much money by sorting out the champaca flowers from the ylang-ylang flowers, as in some localities both classes of trees grow in the same grove. This idea is also erroneous.

(1907) was late, so that distillation was not begun on any large scale until August (1907) and it then extended into February (1908).

Large numbers of ylang-ylang trees grow in many of the provinces; in the Camarines, Mindoro, and Albay there are stills, and in Bohol there are many trees, but as yet no stills. The trees are also probably found in quantities in many of the other provinces, where oil is not yet distilled.

The impression is very general in Manila that the provincial flowers are inferior and will not make good oil. This opinion is no doubt largely due to the lower quality of provincial oils caused by poor distillation. There is every reason to believe that the flowers are just as good in the provinces as in the region around Manila, especially in those regions where the trees are cultivated and raised on a large scale. Some firms in Manila distill oil in the provinces, and the prices which they obtain are just as high as those derived from their Manila product. Moreover, the provincial distiller has two very decided advantages over his Manila competitors in that the price which he pays for flowers is lower (12 to 20 centavos, Philippine currency, per kilo), and in that he can refuse to accept poor flowers, as the competition is not so keen. The next advance for the industry would seem to be the installation of first-class apparatus and the introduction of correct distillation methods in the provinces.

METHODS OF DISTILLATION.

Much mystery surrounds the distillation of the oil of ylang-ylang in Manila. The manufacturers are supposed to have valuable trade secrets, so that no one is allowed to visit the distilleries of many of them. However, I have been inside of some of the Manila distilleries where no such restrictions exist and have also distilled the first quality of ylang-ylang oil in this laboratory. I do not wish to violate any confidence imposed in me by the manufacturers who have allowed me to visit their plants and have told me of their methods of distillation, but I do not believe there are any trade secrets; by this I do not mean to imply that any one can distill first quality ylang-ylang oil, but with the proper apparatus an operator who thoroughly understands the distillation of essential oils in general will soon find out the special small points in the distillation of ylang-ylang oil. The important points where many err, and this is especially true of the provincial distillers, is in the wrong choice of fractions, in burning the flowers and in obtaining too much resin in the oil. The oil must be distilled slowly, with *clean steam*, the flowers being so placed in the stills as to avoid their being cut into channels by the steam. The quantity of the oil taken is only a fraction of the total amount in the flowers. Disregard of this factor is one of the most grievous errors of the provincial distillers, for, on the contrary, they are usually too anxious to obtain a large yield of oil, and therefore they will

often distill 1 kilo from 150 to 200 kilos of flowers. The quantity of the latter to be taken to produce 1 kilo of oil naturally varies with their quality, but in general the amount should be 300 to 500 kilos, probably averaging about 400. After the first quality oil has been distilled, then a varying quantity of the second grade, up to a volume equal to that of the first, may be obtained from the same lot of flowers; after this operation the still and condensers must be thoroughly cleaned and steamed out to prevent contamination of the next distillation of first-quality oil with the remains of the second quality adhering to the apparatus. The distiller usually judges of the time to change the receptacle from that used for first quality to that employed for the second, by taking note of the odor of the distillate. The oil is received in some type of Florence flask, usually two or more of these are connected in series and the condensed water is used in future distillations. The whole apparatus is best lined with block tin, although some distillers have found nickel to be more satisfactory. The oil, after separating from the water, is clarified and as it is sensitive to light and air, it should be placed into dark colored bottles as soon as possible; these should be filled to the neck, well stoppered and then paraffined to keep out all air. In the ideal apparatus the receivers should be so constructed that very little light and air has access to the oil. The possibilities of vacuum distillation with steam to obtain as large a yield as possible of the fragant lower boiling esters and alcohols and as little as possible of resins and sesquiterpenes, has suggested itself. Some experiments along these lines were undertaken, but the apparatus available was not satisfactory for the purpose owing to losses in the condensers. The maceration of the flowers to allow the oil to escape more easily also suggests itself as a possible improvement in distillation methods. Experiments along these lines will be undertaken at some future time when a new still, adapted to the purpose, has been purchased.

THE ANALYSIS OF YLANG-YLANG OIL.

Ylang-ylang oil does not owe its fragrance to any one substance, but contains a great number of odoriferous compounds, hence it is not possible to value it by certain analytical determinations as is the case with many essential oils. At the present time ylang-ylang oil is largely bought and sold on the judgment of the dealers, the determining factor being the odor, and much prejudice as well as uncertainty of valuation exists. It is highly desirable to have other means of determining the value of the oil. This would be especially advantageous for those Manila houses who purchase oils other than those of their own manufacture, as experience has shown to these firms that the judgment of the purchaser in Manila does not always agree with that of the one in Europe. It is obvious that it is not possible in the present state of our knowledge of ylang-ylang oil to judge of its quality from the analysis alone, but I

believe the following results will show that the ordinary analytical constants are of very great assistance, as only the records of isolated constants obtained on oils largely of unknown origin are available in the literature. Owing to this lack I have determined the simple constants on a number of oils of known origin. Most of the latter were from one distillery, the process of distillation being watched and the samples collected by myself. In this manner I was able to obtain a few analytical constants on oils known to be of first or second grade; the results recorded present many regularities and are so promising that it is hoped, as more material becomes available, to discover other constants, so that in time the purchase and sale of ylang-ylang oil may be placed on an exact analytical basis. In this first series the values determined were: Specific gravity at $\frac{30°}{4°}$ (pyknometer); optical rotation at 30°; refractive index, $N\frac{30}{D}$; and ester number, the latter by the usual method, using 1 gram of oil. The results are tabulated as follows:

TABLE II.—*Tabulation of the constants of first-grade ylang-ylang oils.*

No.	Sp. gr. $\frac{30°}{4°}$	$A\frac{30°}{D}$	$N\frac{30°}{D}$	Ester number.	Origin and remarks.
1	0.941	−43.6	----------	129.7	My distillation, Apr., 1907. First 0.45 per cent from 10 kilos of good flowers.
2	0.920	35.5	1.4846	108	B.'s distillate of Aug. 17, 1907.
3	0.911	-39.3	1.4840	95	First half of first-quality oil distilled Aug. 17, 1907.
4	0.921	-35.1	1.4821	109	B.'s distillate of Aug. 20, 1907.
5	0.939	−34.2	1.4880	131	B.'s distillate of Aug. 22, 1907.
6	0.920	38.9	1.4838	98	B.'s distillate of Aug. 23, 1907.
7	0.925	45.2	1.4900	110	B.'s distillate of Aug. 24, 1907. Typhoons and poor flowers.
8	0.919	−45.9	1.4864	100	B.'s distillate of Aug. 27, 1907. Rains and typhoons.
9	0.912	−48.2	1.4852	90	B.'s distillate of Aug. 29, 1907. Flowers very poor because of continued typhoons.
10	0.922	−26.0	1.4794	117	First quality oil rectified *in vacuo*. B.'s distillate 90 per cent yield.
11	0.915	−45.6	1.4843	96	B.'s distillate of Aug. 31, 1907. Flowers so poor because of continued typhoons that 500 kilos were used for 1 kilo of oil.
12	0.913	−38.3	1.4808	95	B.'s distillate of Sept. 5, 1907. Flowers good as a result of three days' sunshine and hence a large yield of oil.
13	0.924	−49.7	1.4898	104	B.'s distillate of Sept. 7, 1907.
14	0.927	44.4	1.4883	112	B.'s mixed distillate.
15	0.916	−36.9	1.4811	100	B.'s distillate of Sept. 10, 1907.
16	0.915	−33.2	1.4747	102	Distillate 55 grams obtained by redistilling 100 kilos of ylang-ylang condensation water.
17	0.917	39.8	1.4785	96	B.'s distillate of Sept. 12, 1907.
18	0.922	45.9	1.4890	104	B.'s distillate of Sept. 3, 1907.
19	0.921	−40.7	1.4825	108	B.'s mixed distillate.
20	0.914	−37.9	1.4895	101	First-quality oil from Mindoro.
21	0.949	36.1	1.4940	138	Distilled *in vacuo* with steam from selected flowers.
22	0.827	42.2	1.4912	126	B.'s distillate of Feb. 1, 1908, from very good flowers.
23	0.958	−27.0	1.4910	169	0.4 per cent yield from selected flowers with very careful distillation. A very fine oil.

TABLE III.—*Tabulation of the constants of second-grade ylang-ylang oils.*

No.	Sp. gr. $\frac{30°}{4°}$	A $\frac{30°}{D}$	N $\frac{30°}{D}$	Ester number.	Origin and remarks.
1	0.929	—69.2		84.6	Corresponds to No. 1, above. Second 0.42 per cent from same distillation as No. 1.
2	0.910	—27.7		89	First half by distillation *in vacuo* from a provincial oil.
3	0.015	—56.3		42	Second half by distillation *in vacuo* of the same provincial oil.
4	0.910	—27.4		64.1	Provincial oil from Nueva Caceres. Distillate of Mar., 1907.
5	0.912	—51.5		83	My distillation; poor flowers; 0.45 per cent yield.
6	0.921	—55.7		75	My distillation; poor flowers; 0.52 per cent yield.
7	0.940	—38.8		80	My distillation; poor flowers; 0.61 per cent yield.
8	0.918	—42.7	1.4950	84	Provincial oil.
9	0.918	—37.2	1.4954	77.1	Do.
10	0.942	—31.3	1.4978	87	Corresponds to No. 3, Table II. B.'s second-quality oil of Aug. 17, 1907.
11	0.913	—86.0	1.5000	72	Corresponds to No. 4, Table II. B.'s second-quality oil of Aug. 20, 1907.
12	0.917	—66.7	1.5032	70	My distillation of second-quality oil from flowers from which the first quality had been previously distilled. Yield, 0.7 per cent.
13	0.919	—61.4	1.4977	86	Second-quality oil corresponding to No. 5, Table II.
14	0.918	—66.4	1.4986	83	Second-quality oil corresponding to No. 6, Table II.
15	0.903	—81.3	1.4981	59	Second-quality oil corresponding to No. 7, Table II.
16	0.928	—30.2	1.4927	64	Provincial oil.
17	0.918	—73.5	1.4979	80.8	Second-quality oil corresponding to No. 8, Table II.
18	0.906	—76.0	1.4991	67	Second-quality oil corresponding to No. 9, Table II.
19	0.926	—75.0	1.5054	80	Second-quality oil corresponding to No. 11, Table II.
20	0.901	—44.4	1.4935	54	Provincial oil.
21	0.896	—46.8	1.4838	72	Provincial oil No. 20 rectified *in vacuo;* 0.65 per cent yield.
22	0.897	—29.8	1.4788	69	Provincial oil No. 20 rectified *in vacuo;* 0.50 per cent yield.
23	0.914	—84.7	1.5001	73	Second-quality oil corresponding to No. 12, Table II.
24	0.913	—66.8	1.4926	86	Second-grade "Sartorius" brand.[a]
25	0.910	—69.0	1.4972	69	Second-quality oil corresponding to No. 13, Table II.
26	0.904	—87.0	1.4980	68	Second-quality oil corresponding to No. 15, Table II.
27	0.922	—35.8	1.4962	77	Provincial oil.
28	0.926	—51.6	1.5002	89	Do.
29	0.913	—34.3	1.4980	86	Do.
30	0.915	—43.3	1.4962	81	Iriga oil. Approaches first-grade oil in quality.
31	0.921	—36.2	1.5002	94	Oil from Guinobatan, Albay. Approaches first-grade oil in quality.
32	0.914	—55.4	1.5008	82	Second-quality oil from same locality. Same distillation.
33	0.920	—42.6	1.4916	85	Good second-quality oil from B's plant.
34	0.912	—45.6	1.4928	90	Oil from Nueva Caceres. Approaches first-grade in quality.
35	0.908	—30.1	1.5082	53	Oil from Mount Isarog, Ambos Camarines. A very poor oil.
36	0.912	—32.1	1.4942	86	Oil from Albay. Very close to first-grade oil.

[a] The manufacturers of the "Sartorius", one of the best brands of ylang-ylang oil, have refused to sell us any of their first-quality oil, and the analysis of number 24 was made from the second quality of the oil, sold in Manila as "essence of ylang-ylang de Pablo Sartorius." We expect to be able to obtain the first-grade oil from European sources, and hope to include this standard brand in our future work.

DISCUSSION OF ANALYTICAL RESULTS.

Several regularities will at once be noted. The ester number of first-grade oils is usually 100 or more, whereas that of second grade but rarely rises above 80; the refractive index of the former class is usually low, being but rarely over $N\frac{30^\circ}{D}=1.4900$, whereas that of the latter approaches 1.5000. This difference is due to the larger content of sesquiterpenes and resins in second-grade oils, cadinene having a refractive index $N\frac{30^\circ}{D}=1.5060$. The optical rotation of first-grade oils is much lower than that of the second grade, it being but rarely over -45° and usually varying from -32° to -45°, that of the second grade being around -60° and over. This difference is also caused by the high content of the latter in sesquiterpenes. A few provincial oils have a low optical rotation together with a low ester number, and such oils are in general very poor, they are also apt to have a very low specific gravity.[5] The results all go to show that an oil with a low refractive index, low optical rotations, and high ester number is almost certain to be good, while high refractive index, high optical rotation, and low ester number indicate a second-grade oil.

No especial regularities have been noted in the specific gravities of the various oils, save that if an oil has a high specific gravity and high ester content (ester number above 110) it may follow that it may also have a higher refractive index, and oils with all these constants are very superior. (See Table II, number 23.)

Manila buyers of provincial oils are often anxious to ascertain the quantity of flowers used by the distiller in obtaining the oil offered, so that they may judge as to its quality. A number of experiments were made on the distillation of ylang-ylang oil *in vacuo* to obtain data on this point and to ascertain whether it might be possible to rectify a lower grade of oil by such a procedure.

One hundred cubic centimeters of first-quality oil were placed in a 200 cubic centimeter, high-necked flask, the distance from the surface of the oil to the exit tube being 16.5 centimeters; a slow, regular distillation was made from a metal bath the temperature of which was kept 15° to 20° hotter than that of the distilling vapor; the total time consumed in the distillation being one hour and twenty-five minutes.

The original oil gave the following constants: Specific gravity, $\frac{30^\circ}{4^\circ}=0.927$; $A\frac{30^\circ}{D}=-44.4$; $N\frac{30^\circ}{D}=-1.4883$; ester number=117.8.

Fraction number 1.—Fifty-two cubic centimeters at 13 millimeters pressure, passing over between 73° and 100°, temperature of metal bath up to 120°.

[5] Cf. Table III, numbers 4, 9, 16, 21, 27, 35, all of which numbers were known to represent very poor oils.

A perfectly colorless oil of very good odor but lacking the fine, sweetish, soft flavor of the original.

Specific gravity, $\frac{30°}{4°}$ =0.921; A $\frac{30°}{D}$ =21.1; N $\frac{30°}{D}$ =1.4778; ester number=120.

Fraction number 2.—Twenty-five cubic centimeters at 13 millimeters pressure, boiling between 100° and 120°, metal bath up to 135°.

A water-white oil having a burnt odor.

Specific gravity, $\frac{30°}{4°}$ =0.916; N $\frac{30°}{D}$ =1.4890; A $\frac{30°}{D}$ =−68.2; ester number=75.

Fraction number 3.—Fifteen cubic centimeters at 10 millimeters pressure, passing over between 120° and 142°, metal bath up to 155°.

Specific gravity, $\frac{30°}{D}$ =0.910; A $\frac{30°}{D}$ =−97.8; N $\frac{30°}{D}$ =1.5031; ester number=109.

The residue in the distilling flask was 6 cubic centimeters, N 30=1.5435. A dark brown resin, of rather agreeable odor.

Fractions 1, 2, and 3, united, gave 92 per cent of the original oil. This oil was perfectly colorless, but the odor was burnt and not nearly as fine as that of the original oil.

The constants were: Specific gravity, $\frac{30°}{4°}$ =0.918; A $\frac{30°}{D}$ =−46.5; N $\frac{30°}{D}$ = 1.4841; ester number=117.1.

The greater part of the burnt odor was removed by running air through this oil for some time, but this process did not restore the mild, sweetish odor of the original oil. When, during the process of distillation the distillers slightly burn the flowers which they use, the resulting oil is allowed to stand in contact with the air for a day or two, the result being the loss of its burnt odor. I have noted in respect to oils distilled *in vacuo* that those samples distilled in a hydrogen atmosphere always have more of a burnt, or flat odor than have the ones fractioned with the ordinary air capillary. My experience seems to be that the rectification of oils *in vacuo* is not an entire success, as the distillates, although apparently of the same composition as the oil from which they are distilled, seem to lack in perfuming power; this is especially true of the lasting qualities of the odor. These results suggest that the highest boiling parts of the ylang-ylang oil and even the resins, are very probably important constituents of the whole, possibly they help to fix the more volatile, odoriferous portions. I have always been impressed by the peculiarly lasting fragrance of the resinous residues of the distillation of ylang-ylang oils fractioned *in vacuo*.

The distillation of many ylang-ylang-oils *in vacuo* has shown that over 50 per cent of the first quality oil will pass over below 100° at 10 millimeters pressure, and when I have tested poorer oils in this respect I have found the amount of substance volatile below 100° at 10 millimeters which passed over to be proportional to the quantity of flowers used in preparing the oil. Thus one oil distilled from flowers at the yield of 1 kilo for 206 kilos of flowers showed 27 per cent of volatile

constituents under the conditions named, whereas another prepared in the proportion of 1 kilo to 150 kilos of flowers gave 19 per cent.

It follows from this that the distillation test is also of value both in determining the quality of an oil and the proportion of flowers used in preparing it. The only manner in which poor provincial oils may be improved is by redistillation with steam, and this procedure results in large losses. Fractioning with steam *in vacuo* also seems quite promising, although the process is very slow. Oils thus obtained are quite colorless, and by taking suitable fractions a very fair oil may thus be prepared from a product which before treatment was almost unsalable.

The following table illustrates the manner in which the very significant constants of refractive index and ester number vary in the different fractions. The numbers represent the successive fractions obtained at L.'s distillery on the dates given:

TABLE IV.—*Successive fractions of ylang-ylang oil.*

No.	April 9, 1907.		April 11, 1907.			September 21, 1907.	
	$N\frac{30°}{D}$	Ester number.	$N\frac{30°}{D}$	Ester number.	Specific gravity.	$N\frac{30°}{D}$	Ester number.
1	1.4878	163	1.4777	102	0.927	1.4888	165
2	1.4908	149	1.4825	185	0.930	1.4903	167
3	1.1970	105	1.4906	119	0.929	1.4945	145
4	1.512	88	1.4978	91	0.931	1.5003	105
5	1.5050	65	1.4994	83	0.924	1.5035	86
6	1.5057	68	1.5040	55	0.929	1.5029	73
7	1.5041	58	1.5068	60	0.933	1.5030	61
8	----------	----------	1.5083	64	0.940	1.5034	57
9	----------	----------	----------	----------	----------	1.5023	54
10	----------	----------	----------	----------	----------	1.5000	49

A double refined oil (twice distilled) from the same firm gave as follows for the first and second fractions:

1. $N\frac{30°}{D}=1.4921$; specific gravity=0.922; ester number=105.

2. $N\frac{30°}{D}=1.4978$; specific gravity=0.934; ester number=92.

THE ADULTERATION OF YLANG-YLANG OIL.

I do not believe that adulteration of ylang-ylang oil is very general in the Philippines. The common adulterants are said to be alcohol, turpentine, coconut or other fixed oils, and kerosene. When turpentine is used as an adulterant, it is sprinkled over the flowers and then subjected to distillation with the rest and when small quantities are thus used its detection is exceedingly difficult, as pinene has been reported as a normal, lesser constituent of true ylang-ylang oil. The presence of ter-

penes in ylang-ylang oil probably depends upon the fact that unripe flowers in which terpenes are apt to occur are mixed with those used for distilling. I could not find pinene or other terpenes in 100 cubic centimeter samples of oils made from fairly good flowers, but the distillation of very unripe flowers gives an oil which has an odor differing entirely from that of ylang-ylang; on the other hand it resembles that of a mixture of turpentine and bananas, and doubtless it contains quantities of terpenes and of benzyl or amyl (?) acetate.

I have examined a sample of turpentine which was said to be prepared for the use of ylang-ylang distillers; it proved to be a very thoroughly refined, dextro-rotary product, flavored with a trace of essence of peppermint. If turpentine is present in an ylang-ylang oil in any quantity it gives to the latter a sharp, harsh odor, it lowers the specific gravity, optical rotation and refractive index, and it may be detected in the first fraction upon distilling the ylang-ylang oil *in vacuo*. If, upon fractioning a 100 cubic centimeter sample at 10 millimeters pressure, more than 1 cubic centimeter passes over below 65°, turpentine or some other low-boiling adulterant may be at once suspected. The odor of this fraction will often give some clue as to the adulterant which has been used and if it is suspected that this is turpentine, pinene may be tested for in the usual manner. The presence of pinene is best proved by its conversion into the bisnitroso-chloride, which with benzylamine gives the corresponding nitrol benzylamine melting at 123°.

Alcohol is detected in ylang-ylang oil by shaking the sample thoroughly three times with a small amount of water, the latter being thoroughly separated from the oil by centrifugating. The iodoform reaction is then used with the aqueous solution, sodium carbonate and iodine dissolved in potassium iodide being added. I have satisfied myself that pure ylang-ylang oil gives no reaction with these reagents and that 1 per cent of alcohol can be detected in a 20 cubic centimeter sample by this method. Pure ylang-ylang oil will sometimes give a faint reaction. This is no doubt owing to the alcohol which is used in washing the funnels and flasks in the distillery.

Coconut or other fatty oils are detected by the well-known method of placing a drop of the oil on bibulous paper, and this course is satisfactory if the adulterant is present in any quantity. The solubility in 90 per cent alcohol has also been proposed as a test, as fatty oils are soluble with difficulty in alcohol of this strength. I have found that 3 per cent of coconut oil added to an ylang-ylang oil of the first quality could be at once detected by the opalescence produced by treating the mixture with two volumes of 90 per cent alcohol. However, the test, if used indiscriminately is liable to lead to unreliable results, because a pure, second-grade ylang-ylang oil gives a marked opalescence with alcohol of the same strength; this is due to the fact that sesquiterpenes preponderate in this

quality and the latter are insoluble in 90 per cent alcohol. The difference becomes more marked on using 75 per cent alcohol, as the first quality of ylang-ylang oil dissolves in this strength with only a faint opalescence, while second quality separates in large globules; so that this distinction offers an easy method of roughly judging the quality of the oil.

Another method of value is to prepare a 1 per cent solution of the oil in alcohol and compare the odor with a similar one of an oil of known quality, as judgment is much more certain as to the perfuming power when dilute solutions instead of the pure oils are used. One cubic centimeter of each solution can then be poured on separate pieces of bibulous paper, the odor being compared at the end of twelve, twenty-four, or even a longer number of hours; this test gives some idea in regard to the permanence of the odor.

Pure ylang-ylang oil obtained by distillation *in vacuo* leaves a residue of about 5 per cent and of course if fixed oils are present, this will be larger. Moreover, the residue from pure ylang-ylang oil has a refractive index $N\frac{30^\circ}{D}$ of about 1.5400, whereas a product containing 5 per cent of added coconut oil had an index of $N\frac{30^\circ}{D}=1.5000$. Fatty acids can be detected in this residue left on distillation by heating it with fused potassium bisulphate, for if fatty oils are present the odor of fatty acids as well as a marked one of akroleïn is observed. The odor of the fatty acids gives the best sign of their presence in the residue, because pure ylang-ylang oil upon being treated in this way gives a rather sharp odor, which, however, might be mistaken for that of akroleïn. If coconut oil has been added to a first-grade ylang-ylang oil to the amount of 5 per cent it can be detected by the odor alone, if the person making the test is familiar with the oil. Petroleum or mineral oil can be detected in ylang-ylang by destroying everything but these adulterants with concentrated sulphuric acid and then distilling the remainder.

The use of any adulteration is more emphatically the height of commercial folly for ylang-ylang than it is for any other essential oil, for only the product of the highest quality brings a remunerative price. A 10 per cent increase in quantity by means of adulteration may cut the price in two, or may result in an oil which can not be sold at any price. The greatest advance in the ylang-ylang oil industry will take place when the distillers own their groves of trees and can select only ripe, yellow flowers for distillation. This fact is emphasized quite strikingly by the following experiment:

Fifty-four and five-tenths kilos (120 pounds) of extra fine flowers, one-half of which were perfectly yellow and ripe, were distilled with steam in the usual manner and the following fractions were obtained:

Number 1: 55 cubic centimeters; specific gravity, $\frac{30°}{4°}=0.960$; $A\frac{30°}{D}=-19.8°$; $N\frac{30°}{D}=1.4865$; ester number, 178.

Number 2: 33 cubic centimeters; specific gravity, $\frac{30°}{4°}=0.959$; $A\frac{30°}{D}=-26.5°$; $N\frac{30°}{D}=1.4914$; ester number, 160.

Number 3: 90 cubic centimeters; specific gravity, $\frac{30°}{4°}=0.954$; $A\frac{30°}{D}=-34.6°$; $N\frac{30°}{D}=1.4956$; ester number, 154.

Number 4: 80 cubic centimeters; specific gravity, $\frac{30°}{4°}=0.942$; $A\frac{30°}{D}=-53.4°$; $N\frac{30°}{D}=1.5020$; ester number. 113.

Tubes numbers 1, 2 and 3 united gave the following constants: Specific gravity, $\frac{30°}{4°}=0.958$; $A\frac{30°}{D}=-27.0$; $N\frac{30°}{D}=1.4910$; ester number, 169.

The total oil obtained was 258 cubic centimeters, which is 264 grams, corresponding to a yield of 0.45 per cent.

This yield was nearly twice the normal amount and the quality of the oil was very high, as was shown not only by the analytical figures given above, but also was confirmed by the opinions of Manila experts to whom it was submitted.

I believe these experiments indicate that 200 kilos of ripe, yellow flowers will give 1 kilo of a better quality of oil than will 400 kilos of the class of poor, mixed flowers used at the present time. It is a well-known fact of plant physiology that the odoriferous substance is present in the flower in greatest abundance and in finest quality at the time when it is mature and ready for pollination. No doubt, in the course of time much can be done toward improving the yield and quality of ylang-ylang oil by intelligent plant selection. Such work requires much patience and at present there are absolutely no data available save a general opinion that the ylang-ylang trees of the wild mountain regions are not as fragrant as the cultivated ones of the lowlands.

Fifty-four and five-tenths kilos of the same flowers were also distilled in a vacuum of 100 millimeters, an exceedingly slow operation. There were obtained 32 cubic centimeters of oil of a very good quality, with the following properties: Specific gravity, $\frac{30°}{4°}=0.949$; $A\frac{30°}{D}=36.1$; $N\frac{30°}{D}=1.4940$; ester number, 138.

The low yield is due to the fact that the only apparatus available had the vacuum pipe opening directly into the oil receiver, with only a comparatively short condenser above, and as a consequence most of the oil was lost by volatilization.

THE COMPOSITION OF YLANG-YLANG OIL.

The chemical composition of ylang-ylang oil has been pretty well established through the labors of many chemists.

Gal[6] found no aldehydes or ketones, but benzoic acid as esters of unknown alcohols. Flückiger,[7] correctly names the tree from which ylang-ylang oil is obtained and gives a good historical résumé concerning the oil and its introduction into Europe. He found in the oil a very small amount of benzoic acid, acetic acid and unidentified phenols (from the color reactions with ferric chloride) and suspected the presence of an aldehyde or ketone.

He obtained a very small amount of a precipitate with sodium bisulphite. He was unable to identify any of the alcohols from the oil. There would seem to be some doubt as to whether Flückiger studied a genuine sample of ylang-ylang oil, as the esters of benzoic acid are so abundantly present that the acid is separated in quantity with the greatest of ease. Reychler[8] found benzoic and acetic acids, linaloöl, geraniol and cadinene. Darzens[9] found methyl alcohol, *para*-kresol, benzoic and acetic acids and considered that the *para*-kresol was present as the acetate, for he states that *para*-kresol acetate has an odor somewhat like that of ylang-ylang oil. The final and most exhaustive researches on this perfume oil are due to the commercial houses, especially to Schimmel & Company,[10] whose results are embodied in a patent for artificial ylang-ylang oil.

A rational method of analysis of this oil should, if possible, be founded on its composition, and therefore we have undertaken studies in this direction and have succeeded in adding two new substances, formic acid and safrol (isosafrol), to the list of the known constituents of the ylang-ylang oil.

Experiment 1.—One hundred grams of first-grade ylang-ylang oil were taken; its constants were as follows: Specific gravity, $\frac{30^\circ}{4^\circ}=0.921$; $A\frac{30^\circ}{D}=-40.7$; $N\frac{30^\circ}{D}=1.4825$; ester number, 108.

This oil gave only a very faint reaction with ferric chloride at the contact zone, due to methyl salicylate, showing that the phenols were combined. It is interesting to note that none of the oils I have handled gave a strong color reaction with ferric chloride, and therefore the possibility suggests itself that the ageing of the oil causes a small amount of hydrolysis of the phenol-ethers, for most European observers have obtained pronounced color reactions with ferric chloride. The oil I used was more than neutralized with 0.1 cubic centimeter of $\frac{N}{10}$ caustic soda. All good ylang-ylang oils are neutral.

The oil was heated to 100° in a sealed tube with 15 grams of sodium hydroxide, dissolved in 30 cubic centimeters of water, for eight hours. At the end of this time a considerable amount of solid has separated; there was no pressure in the tube. The contents was dissolved in water and ether, the etherial layer separated,

[6] *Compt. rend. Acad. d. sc., Par.* (1873), **76**, 1482.

[7] *Arch. d. Pharm.* (1885), **18**, 24.

[8] *Bull. Soc. Chim.* Paris (1894), **11**, 407, 546, 1057.

[9] *Ibid.* (1897), **27**, 83.

[10] D. R. P. 142, 859 Class 23, *a*. Schimmel & Company, semiannual report, October 1901 (English edition), p. 53.

the aqueous portion well shaken with ether and the ether several times shaken out with small amounts of water so as to separate the alcohols soluble in that medium, the water being always added to the original alkaline solution. The latter was now distilled with steam and the distillate treated with benzoyl chloride according to Baumann-Schotten, 1.2 grams of methyl benzoate being obtained in this manner. A slight excess of dilute sulphuric acid was now added to the alkaline solution in the distilling flask and the whole was then extracted with ether, the latter being shaken out with small portions of water to remove acids soluble in that medium, these extracts being added to the aqueous portions. This was now distilled with steam, the distillate on titration with standard alkali showed 5.54 grams of volatile acids calculated as acetic. The barium and silver salts of the acids were prepared from this distillate and analysed.

I. 0.6916 grams barium salt gave 0.6466 gram barium sulphate.
II. 0.5195 grams barium salt gave 0.4872 gram barium sulphate.

	Found (per cent).	Calculated (per cent) for $Ba(C_2H_3O_2)_2 2H_2O$	Calculated (per cent) for $Ba(CHO_2)_2$
I. Ba.	55.06	48.7	60.7
II. Ba.	55.10	.....	.....

I. 0.2065 grams silver salt gave 0.1897 gram AgCl
II. 0.2050 grams silver salt gave 0.1885 gram AgCl

	Found (per cent)	Calculated (per cent) for $AgC_2H_3O_2$	Calculated (per cent) for $AgCHO_2$
I. Ag.	69.1	64.6	70.58
II. Ag.	69.1	.....	.....

This aqueous solution of the acids reduces potassium permanganate at once, and readily converts mercuric to mercurous chloride. These results, taken in conjunction with the analytical data and the fact that it was impossible to obtain a white silver salt, leave no doubt but that formic acid was present. The figures obtained for the silver salt are naturally different from those for the barium compound because of the slight reduction to metallic silver caused by the formic acid.

The etherial solution containing the acids not soluble in water was now repeatedly extracted with small portions of a solution of sodium carbonate. In this manner there were isolated 9.6 grams of solid acids having the appearance of benzoic and giving a test for salicylic acid with ferric chloride. The benzoic and salicylic acids were separated by conversion of the salicylic acid into the very insoluble dibromsalicylic acid, 0.6 gram, melting at 221° (found, bromine, 57 per cent; calculated, 57.4 per cent) sufficient water being used to keep the benzoic acid in solution.[11] The remaining acid, after extraction and one crystallization from ligroin was 7.7 grams of pure benzoic acid melting at 121° to 122°. After removing the acids, 0.9 gram of phenols having an odor resembling that of isoeugenol and giving a green color with ferric chloride was isolated.

A methoxyl determination according to Zeisel gave the following numbers: 0.92 gram of oil gave 0.1405 gram silver iodide equivalent to 0.031 grams of CH_3. This would represent 0.99 per cent of the total oil or 0.66 grams CH_3OH which would give 2.02 per cent of the total oil as CH_3OH. It would require 2.5 grams

[11] Sharpe: *Ztsch. f. An. Chem.* (1893), **32**, 107.

of CH_3OH to form the methyl esters with the 9.6 grams of solid acids which were found.

The neutral portion of the saponification product distilled *in vacuo* gave the following fractions:

Number 1: 37 grams; B. P. 90° to 120° at 37 mm., $A\frac{30°}{D}=-16.5$; $N\frac{30°}{D}=1.478$.

Number 2: 15.5 grams; B. P. 120° to 130° at 34 mm.; $A\frac{30°}{D}=-31.2°$; $N\frac{30°}{D}=1.4797$.

Number 3: 17.5 grams; B. P. 130° to 150° at 30 mm.; $A\frac{30°}{D}=-77.7°$; $N\frac{30°}{D}=1.4943$.

Number 4: 9.5 grams of resinous residue.

Treatment of fraction 1 with dilute, aqueous potassium permanganate gives benzoic acid melting at 122°, thus proving the presence of benzyl alcohol in this fraction.

The above results gave the composition of ylang-ylang oil as follows:

Component.	Per cent.
Neutral	81.50
Formic and acetic acids	5.54
Benzoic acid	9.00
Salicylic acid	0.60
Methyl alcohol	2.02
Total	99.56

Several attempts were made to isolate an aldehyde from ylang-ylang oil, as treatment of the oil with fuchsine and sulphur dioxide gave the color change characteristic of aldehydes, but phenylhydrazine shows no trace of reaction with the oil and on shaking thoroughly with freshly prepared and very active sodium bisulphite no such bodies could be isolated by the usual means; so that no more than a trace of aldehydes can be present in ylang-ylang oil. The work with 100 cubic centimeters was repeated with 1,000 grams of ylang-ylang oil in the hope that the decomposition of larger quantities would lead to the discovery of constituents heretofore not recognized.

Experiment 2.—One thousand grams of good quality ylang-ylang oil from Nueva Caceres and having the following constants: Specific gravity, $\frac{30°}{4°}=0.912$; $A\frac{30°}{D}=-45.6°$; $N\frac{30°}{D}=1.4920$; ester number, 100, were used.

The oil was saponified in four lots, the first three by using 200 cubic centimeters of oil and 35 grams of potassium hydroxide dissolved in 150 cubic centimeters of 92 per cent alcohol the final one of 497 cubic centimeters of oil was hydrolyzed with 60 grams of potassium hydroxide dissolved in 400 cubic centimeters of the same solvent. Within a few minutes after the alcoholic potash was added the oil became filled with crystals of the potassium salts of the acids. No other solids separate. This was proved by a special experiment with a

sample of first quality oil in which the solid formed by saponification was filtered, well washed with absolute ether and decomposed by dilute acids, the resulting substances being benzoic, salicylic, formic and acetic acids as well as a very small quantity of phenols.

The contents of the first three flasks were completely saponified by two hours' heating on the steam bath with a reflux condenser, the last fraction by one week's standing at room temperature. The procedure used in working up the product was like that given in the details of experiment 1.

The solid, acid portion: The total amount was 91 grams. The benzoic and salicylic acids were separated by means of their esters, salicylic methyl-ester being soluble in a 10 per cent sodium hydroxide solution. The methyl esters after this separation, boiled almost constantly at 195° and 224°, respectively, so that there would seem to be no reason to suspect any acids other than benzoic and salicylic to be present in the solid, acid portion. The total quantities were 6 grams of salicylic acid and 85 of benzoic.

The soluble acid portion: The alkaline, aqueous solution was first evaporated to a small bulk in order to remove all neutral volatile substances. It was then rendered acid with dilute sulphuric acid, and the volatile acids were distilled. The total volatile acids, calculated as acetic acid, were 63.5 grams. Barium salts were prepared and gave the following analytical data:

0.6995 gram barium salt gave 0.6521 gram barium sulphate

	Found (per cent).	Calculated (per cent) for $Ba(C_2H_3O_2)2H_2O$	Calculated (per cent) for $Ba(HCO_2)_2$
Ba	54.97	48.70	60.3

Naturally, the percentage of barium found gives no clue to the relative proportions of the two acids present because of the differing solubilities of the salts, the acetate of barium being more soluble in water than the formate. The solution of the soluble acids reduces potassium permanganate and also mercuric chloride, and as neutral salts have been prepared from the solution with a greater percentage content of barium than is in the acetate, the only conclusion is that formic acid is present.

The formic acid was estimated according to the method of H. C. Jones[12] by heating with an excess of standard potassium permanganate in the presence of an alkaline carbonate, then adding a known excess of oxalic acid, and titrating back with potassium permanganate. The result showed that from the original kilo of oil there were separated 41.2 grams of acetic and 17.1 grams of formic acid.

A portion of the barium salts of these acids was treated with ethyl alcohol and concentrated sulphuric acid; the resulting esters possessed the characteristic odor of ethyl acetate and formate and no odor was noted suggesting the presence of acids other than those named. Reychler[13] states that he has observed a pronounced, rancid odor in the aqueous mother liquors, suggesting small amounts of the higher fatty acids. I could confirm his observation and I believe there is a trace of valerianic acid in the mother liquor.

The phenol fraction.—This was in all 10 grams. The phenols gave a green color with ferric chloride and an odor resembling that of kreosol (the 3-methyl ether of homopyrocatechin ($C_6H_3(CH_3)^1(OCH_3)^3(OH)^4$) was noted in this fraction. There was separated from this fraction according to the method of Baumann-Schotten by the action of benzoyl chloride a small amount of *para*-kresol ben-

[12] *Am. Chem. J.* (1895), 17, 539.

[13] *Loc. cit.*

zoate, melting at 77° and isoeugenol is also present. I have not attempted thoroughly to study the phenol fraction because of its small amount and because it has been well identified by Schimmel & Company.[14]

The neutral fractions after shaking out the alcohol as thoroughly as possible, was dried over anhydrous sodium sulphate, as calcium chloride was difficult to remove, both because of the presence of ethyl alcohol and because of the solid compounds which may be formed with benzyl alcohol and with geraniol.

The total neutral oil weighed 808 grams; it was subjected to three careful fractionations *in vacuo*, using a column of glass beads in a high-necked distilling flask. The fractions obtained, together with their physical constants, are given in the following table:[15]

TABLE V.—*Fractions obtained by distilling the neutral oils left after saponifying 1,000 grams of ylang-ylang oil and removing other constituents.*

No.	Boiling point.		Sp. gr. $\frac{25°}{4}$	A $\frac{25°}{D}$	N $\frac{25°}{D}$	Amount (grams).	Percentage of hydroxyl.
	15 mm.	760 mm.					
1	57°- 68°	160°-170°	0.880	+11.5	1.4807	8.1	0.5
2	68°- 75°	170°-175°	0.903	+ 1.2	1.4851	17.6	1.4
3	75°- 80°	175°-180°	0.913	— 5	1.4850	16.4	2.2
4	80°- 85°	180°-185°	0.902	— 8.9	1.4803	19.1	8
5	85°- 90°	185°-190°	0.889	—12.8	1.4750	18.3	11.07
6	90°- 95°		0.8885	—15.4	1.4750	71	11.6
7	95°- 98°		0.8895	—15	1.4764	124	11.6
8	98°-105°		0.9131	—11.7	1.4862	25	11.2
9	105°-115°		0.9045	—10.5	1.4869	32	10.3
10	115°-125°		0.8894	—24.2	1.4896	61	8.4
11	125°-130°		0.9065	—64.4	1.5060	79	0.5
12	130° (con.)		0.8926	—74.4	1.5055	117	0.13
	Total except residue					588.5	
13	Residue, pleasant smelling tar and polyterpenes					172.0	
	Total					760.5	

[14] *Loc. cit.*

[15] This method of fractionation with a column of glass beads has been used by Michael and by Freer for many years and gives exceedingly satisfactory results. For a small flask, a test tube is drawn out to a capillary and the upper end so cut off as to rest rather snugly in the neck of the distilling flask. Glass beads are then filled in to within 1 or 2 centimeters of the exit tube. A properly prepared tube gives a continuous stream of small bubbles from its capillary end because of the small reservoir just below the glass beads, so that the distillation *in vacuo* proceeds smoothly and without bumping. If it is desired to introduce a stream of air or other gas through a capillary, as it is advisable to do when dealing with large quantities of oils, the beads rest on a piece of platinum gauze supported by a test tube or suitable bent rod. The separation effected by the glass beads because of the many points of glass contact is surprisingly efficient, probably better than with bulb forms of fractioning apparatus, and the vapor does not need to be driven nearly as high as with the older forms of apparatus.

The figures given for the percentage of hydroxyl in the seventh column of the table were obtained by the Grignard reaction, in accordance with the method proposed by Zerewitinoff.[16] In using this method, methyl iodide dissolved in amyl ether is treated with magnesium and the amount of methane given off by adding an alcohol to the resulting magnesium methyl iodide is measured. This represents the amount of hydroxyl in the added compound, the reaction being:

$$ROH + CH_3MgI \longrightarrow CH_4 + ROMgI.$$

The method is exceedingly convenient after the reagent is prepared, it is quick and uses only about 0.2 gram of oil. It bids fair to displace the older method of obtaining the acetyl number. It is well known that with many alcohols, as for example with linaloöl, the standard methods give an acetyl number many percent too low. This new method promises to give more accurate numbers and is so exceedingly convenient that we are now testing it thoroughly. The results I have obtained in my first series are as follows:

	Found hydroxyl (per cent).	Calcuted hydroxyl (per cent).
Linaloöl	10.95	11.04
	11.4	
	11.2	
	11.3	
	11.1	
	11.1	
Geraniol	11.3	11.04
	11.4	
	11.2	
Benzyl alcohol	15.8	15.74
	15.7	
	15.9	
	15.6	

The formula used in calculating the percentage of hydroxyl is as follows:

$$X \text{ (per cent OH)} = 0.0764 \frac{V}{S}$$

where V = volume of CH_4 at 0° and 760 millimeters and S is the weight of substance taken.

Fraction 1 always presented an odor very much resembling that of amyl or hexyl alcohol. By treating this fraction with benzoyl chloride according to the method of Baumann-Schotten and redistilling *in vacuo*, this odor is removed, the fraction then assumes the odor of terpenes and I was able to obtain a few crystals of pinene nitrosylchloride melting at 103° from this low-boiling portion. This, together with the optical rotation of this fraction would indicate the presence of *d*-pinene in small quantity. The boiling point of the first three fractions indicates that very little pinene is present. A very small percentage of hydroxyl was also found, so that the major part probably consists of other terpenes. The presence of limonene could not be proved. As these terpenes are of no great importance in determining the odor of ylang-ylang oil, no further attempts were made to identify them.

[16] *Ber. d. chem. Ges.* (1901), 40, 2023.

Fractions 1 to 5 seem to consist of a mixture of terpenes with linaloöl and benzyl alcohol, with possibly a small amount of amyl or hexyl alcohol. A special experiment made to separate the terpenes from the alcohols by means of the Grignard method according to the equation

$$CH_3MgI + C_{10}H_{18}OH \rightarrow C_{10}H_{18}OMgI + CH_4$$

demonstrated that linaloöl as well as the alcohols of ylang-ylang oil give addition products which are soluble in ether, so that no separation was possible.

Fractions 6 and 7.—These fractions possess an odor much like that of linaloöl and in addition another, sweet one, is present. Oxidation of 9 grams of the united fraction with dilute potassium permanganate gave 1.2 grams of benzoic acid melting at 121°. This corresponds to 13.3 per cent of benzyl alcohol.

A small portion of these fractions was oxidized with potassium bichromate and dilute sulphuric acid, and by this means the odors of benzaldehyde and of citral were obtained.

The fractions 6 and 7 were also heated with finely powdered calcium chloride for one hour on a steam bath and then kept in a cool place for twenty-four hours. A solid compound with calcium chloride separated, this was filtered with the aid of a pump, and well washed with ether. Twenty-nine grams of an oil boiling between 200° and 206° at ordinary pressure were obtained on decomposing this addition product with water. This body had the odor of benzyl alcohol and proved to be the latter almost in its entirety by conversion into benzyl acetate, and also by obtaining an 85 per cent yield of benzoic acid by oxidation. The liquid not entering into combination with calcium chloride, proved itself to be almost pure linaloöl, as is shown by the following constants: Specific gravity, $\frac{30°}{4°}=0.8586$; $A\frac{30°}{D}=-16°$; $N\frac{30°}{D}=1.4655$; boiling point 190° to 195° at ordinary pressure. The odor of this portion was identical with that of linaloöl, and citral was produced from it by oxidation with potassium bichromate.

Fraction 8.—This portion was separated into 10 grams of benzyl alcohol, 11 grams of linaloöl, and 3 grams of an oil which solidified with calcium chloride, boiled at a higher point than benzyl alcohol and therefore from its odor and the formation of an addition product with calcium chloride it was determined to be geraniol.

Fraction 9.—This fraction, on treatment with powdered calcium chloride immediately became hot and solid. This method of separation gave 8 grams of an oil not acted upon by calcium chloride and having a refractive index of $N\frac{30°}{D}=1.5131$. This portion had the odor of safrol. Oxidization with acid potassium bichromate gave the odor of heliotrope. The oil which was separated from the calcium chloride compound possessed a pronounced geraniol odor, boiled at 108° to 115° at 10 millimeters; specific gravity $\frac{30°}{4°}=0.881$; $N\frac{30°}{D}=1.4821$.

Fraction 10 was similarly separated into 12 grams of geraniol, a small amount of safrol, and into sesquiterpenes.

Fractions 11 and 12 consisted almost entirely of sesquiterpenes, among which cadinene is present, as a small yield of cadinene hydrochloride melting at 117° was obtained on treating 10 grams of this fraction, dissolved in ether, with dry hydrogen chloride.

SUMMARY OF RESULTS.

Ylang-ylang oil is thus seen to contain the following substances: Formic, acetic, valerianic (?), benzoic and salicylic acids, all as esters; methyl and benzyl alcohols; pinene and other terpenes, linaloöl, geraniol, safrol, cadinene and other sesquiterpenes; eugenol, isoeugenol, *p*-kresol, probably as methyl ethers; and kreosol.

Many of the esters which could possibly be formed by a combination of the isolated alcohols and acids have been prepared in this laboratory in order to become familiar with their properties and especially with their odor. It seems of interest to give notes in regard to their properties.

Benzyl salicylate.—No record appears in the literature of the preparation of this compound. It is made as follows: 27.4 grams of salicylic acid are neutralized with 11.2 grams of potassium hydroxide and the solution evaporated to dryness. This potassium salt is heated to 200° for four hours in sealed tube with 25 grams of salicylic acid and 25.2 grams of benzyl chloride. On opening the tube no pressure is observed and all of the benzyl chloride has disappeared. There is obtained 26 grams of a colorless, viscous oil boiling between 186° and 188° at 10 millimeters. The odor is slightly aromatic and pleasant, but not powerful. The oil, after three months in the ice box, has not solidified. Five grams of the ester saponified with alcoholic caustic potash, gave 2.4 grams of salicylic acid melting at 155° (recrystallized from water), and the acid was further identified by conversion into the methyl ester. There also resulted 2 grams of benzyl alcohol, boiling at 204° and converted into benzyl acetate.

Benzyl benzoate has been prepared by the action of sodium benzylate on benzaldehyde. The method used in this laboratory was as follows: 50 grams of sodium benzoate, 50 grams benzoic acid, and 43 grams of benzyl chloride were heated on a reflux condenser in a metal bath at a temperature of 200° for two hours. There resulted 46 grams of oil boiling between 315° and 320°. Benzyl valerianate and benzyl butyrate were also prepared by the same general method, the yield being very good. The method formerly in use, which employed the lead salts, did not give good results.

Benzyl valerianate can also be prepared in almost quantitative yield by the action of valeryl chloride on sodium benzylate. The properties of this body correspond to those given in the literature. The odor of this ester is not as sweet as is that of benzyl acetate, it being more like that of fruit. It is almost certain that there are traces of benzyl valerianate in ylang-ylang oil.

Benzyl-methyl ether is obtained in almost quantitative yield by heating benzyl chloride with a slight excess of sodium methylate dissolved in methyl alcohol, in a sealed tube to 120° for two hours. The transformation is not complete if these same substances are heated only in an oil bath on a reflux condenser, and in addition the benzyl-methyl ether always contains chlorine.

Benzyl-methyl ether is a colorless oil boiling between 166° and 168°; it has an almost nauseatingly sweet odor. There is probably a very small amount of it present in ylang-ylang oil.

Benzyl formate.—Benzyl chloride is heated with a slight excess of potassium formate dissolved in formic acid in a sealed tube at 140° for two hours. The body boils at 84° to 85° at 10 millimeters pressure and has an odor sweeter than that of benzyl acetate, but much like it. The yield is over 90 per cent by this method. It is necessary to use a sealed tube, as benzyl chloride does not dissolve in absolute formic acid at 100°.

Geraniol-methyl ether.—This body was prepared from the sodium derivative of geraniol and methyl iodide. It is a colorless oil, boiling between 100° and 105° at 10 millimeters and at 208° to 212° at ordinary pressure. Its odor resembles that of geraniol, but it is more like that of grass.

Linaloöl-methyl ether is prepared in the same manner as geraniol-methyl ether, it boils between 189° and 192°, and its odor is not very different from that of linaloöl, it is not as fragrant as that substance.

Geraniol benzoate was prepared by the Baumann-Schotten method, using 10 grams of geraniol and 10 grams of benzoyl chloride. The oil boils between 198° and 200° at 15 millimeters. It has quite a pleasant odor, much like that of some of the higher boiling fractions of ylang-ylang oil.

SYNTHESIS OF YLANG-YLANG OIL.

An attempt was made to prepare an artificial product to test the accuracy of these studies on the composition of ylang-ylang oil. The following substances were used:

Methyl benzoate; benzyl acetate and formate; benzyl methyl ether (trace); benzyl valerianate (trace); methyl salicylate; benzyl benzoate; cadinene; safrol; isoeugenol-methyl ether; eugenol; kreosol; methyl anthranilate (trace); *p*-kresol-methyl ether; *p*-kresol acetate.

With these ingredients a mixture was compounded smelling deceptively like good ylang-ylang oil. The fluorescence of ylang-ylang oil, which is always present to a greater or lesser degree, is probably due to the presence of methyl anthranilate.

The above work, and that of others demonstrates that ylang-ylang oil has a composite odor, derived from that of many constituents. While it is possible to make a very good artificial ylang-ylang oil, I do not believe that distillers of the best quality of ylang-ylang oil have much to fear from this competition, as the odor of a first-class oil seems to have more permanence than that of the artificial product. This is a result, I believe, of the presence of sesquiterpene alcohols and fragrant resins in the former.

Work on the physical constants and methods of analysis of ylang-ylang oil will be continued as fast as material is available. The future determinations, in addition to the constants given in this paper will include the acetyl number, and if possible a phenol number. The acetyl number is undoubtedly of much importance, as is evidenced from the large percentage of fragrant alcohols found in ylang-ylang oil. Our first quality of oil gave an acetyl number of 74, while a second quality only gave one of 42. We will also in our future work use a constant equal to the sum of the ester and acetyl numbers, thus representing the total amount of alcohols and esters in the oils. Such a number for the last mentioned first quality oil was 174 as compared to 110 for the second grade product. We believe we will thus be able from a few simple analytical determinations to draw many conclusions as to the composition of any ylang-ylang oil presented to us and thus be able to judge of its quality.

THE COMPOSITION OF HORLICK'S MALTED MILK.

By GEORGE F. RICHMOND and W. E. MUSGRAVE.
(From the Chemical and Biological Laboratories, Bureau of Science.)

Since the publication of our monograph [1] on "Infant Feeding and its Influence upon Infant Mortality in the Philippine Islands" our attention has been directed to errors in the quoted analysis of Horlick's malted milk given on pages 375 and 378 and also our observation on page 374 that the greatest objection to malted milks as infant foods lies in the large amount of insoluble carbohydrates which they contain. The analysis of Horlick's malted milk therein quoted was taken from Chapin [2] who in turn quotes McGill,[3] who reported upon 103 samples representing 22 different brands of infant and invalid foods as found on the Canadian market. His results upon the malted milk in question are the mean of nine separate analyses made by himself and others and are as follows:

	Per cent.
Moisture	2.55
Fat by petroleum ether	1.41
Loss to alcohol and water	63.87
Total albuminoids N×6.25	14.00
Starch fiber, ash, etc., by difference	15.68
Ash	3.57

The manufacturers of Horlick's malted milk maintain, first, that the percentage of fat, 1.41, as quoted is grossly in error and refer to analyses by Smith [4] who found over six times as much, namely, 8.75 per cent, Chittenden [5] who encountered at least 8 per cent, and to European workers, including the British Analytical Control and the Glasgow Corporation, who reported 8.85 and 8.8 per cent respectively; second, that the proteid content, 14 per cent, as found by McGill is also below the true value of 16 to 17 per cent claimed and based upon the analyses covered by the above references; third, that 0.05 per cent represents more nearly the true content of insoluble carbohydrates in their product. Manifestly

[1] *This Jour. Sec. B* (1907), **2**, 4.
[2] Theory and Practice of Infant Feeding, 2d ed. 1904.
[3] Bull. **59**, Laby. Int. Rev. Dept., Canada.
[4] Holt on Infancy and Childhood, 1902.
[5] *Dietetic and Hygiene Gazette*, 1896.

such variation in the percentages of the important ingredients of an established food stuff are well worth inquiry. In the interest of fairness to the manufacturers and ourselves, therefore, we determined to make a personal examination of the product as found on the Manila market.

It has been known for some time that Adam's Soxhlett extraction method for the estimation of fats failed in the presence of considerable quantities of carbohydrates and that some other method of procedure was necessary in order to obtain a maximum yield of fat in sweetened condensed milks, milk powders and malted milks. Modifications of the Soxhlett method such as drying a highly diluted aqueous solution of the material on large surfaces, interstratifying the dried powder with some inert substance such as sand or asbestos or finely grinding the dried powder with powdered glass, before extraction with organic solvents, will increase the yield somewhat. The percentage of fat in Horlick's malted milk determined in this laboratory both before and after grinding the dried powder with powdered glass was 1.78 and 2.50 per cent respectively. The well-known Babcock volumetric method is also not suitable for such products because of the charring action of concentrated sulphuric acid on the carbohydrates. Leach's [6] modification of the Babcock process, which consists in separating the sugars from the fats and proteids by means of copper sulphate before the addition of sulphuric acid, is not very satisfactory when applied to malted milks because of the difficulty of accurately sampling the material and in reading the volume of fat obtained.

Several trials on Horlick's malted milk with Leach's modification of the Babcock process gave an average of 8.32 per cent of fat.

Cochran,[7] with a modified Babcock bottle and by the use of equal volumes of 80 per cent acetic acid and concentrated sulphuric acid, claims that the charring action is much less than when concentrated sulphuric acid is used alone. Instead of centrifugating he separates the fat by means of ether, which is evaporated before the volume of fat is taken. Here again the same difficulties in introducing a very hygroscopic powder into the narrow-neck flask and in reading the correct volume of fat are encountered. However, it is only fair to state that our attempts to obtain concordant results with Cochran's method were made with the ordinary Babcock bottle which does not provide for sufficient means of escape of the ether vapor. In this laboratory much better results were obtained by precipitating the proteids in malted milk with acetic acid and heat and by subsequent extraction of the dry precipitate with petroleum ether.

Our exact procedure was as follows: A 1-gram sample of the air-dry powder was transfered to a small breaker, 25 cubic centimeters of water added and the whole stirred to a completely homogeneous solution. It

[6] *Jour. Am. Chem. Soc.* (1900), 22, 589.
[7] *Jour. Am. Chem. Soc.* (1905), 27, 906.

was then acidulated with 5 cubic centimeters of 1 per cent acetic acid and heated on a steam bath until the albuminoids separated in coarse floccules, after which it was filtered through a weighed platinum Gooch crucible and washed with water until the washings were free from carbohydrates. After drying, the crucible and its contents were transfered to a direct extraction apparatus and exhausted with pretroleum ether, The fat was then determined from the loss of weight of the crucible or from the weight of the petroleum ether extract. A mean of four determinations by this method gave 8.18 per cent of fat. That all the fat is carried down and retained in the Gooch was evidenced by negative tests for fat in the clear filtrate.

Trillat and Sauton [8] have described a new method for the determination of proteids in milk which is identical with the procedure given above for the determination of fat, with the exception that they add 5 drops of commercial formaldehyde to the diluted milk before acidulating with acetic acid, they also extract the dried precipitate with acetone instead of ether. They claim that no proteids could be detected in the filtrate by any of the ordinary reagents.

It was hoped that the process as followed would also serve for the estimation of the total albuminoids in malted milks, but it was found that the filtrate contained at least one-half of the total proteids of the original powder, furthermore that the fat-free residue left in the Gooch crucible contained about 2½ per cent of nonnitrogenous matter calculated on the original weight of malted milk dissolved. The nonnitrogenous matter thus found was not due to incomplete removal of soluble carbohydrates, nor was it mineral in nature, for the ash content of the filtrate accounted for the total amount of ash found in the malted milk by direct estimation; therefore, malted milk undoubtedly contains nonnitrogenous organic matter insoluble in excess of boiling acidulated water to that extent.

The detailed results of our analysis of Horlick's malted milk is given in the following table and represents the mean of four separate analyses:

	Per cent.
Moisture (loss at 100° C.)	4.03
Fat (by petroleum ether)	8.18
Total albuminoids nitrogen×6.25	16.64
Total soluble carbohydrates (loss to boiling water)	64.47
Insoluble nonproteid organic matter, starch fiber, etc.	2.60
Mineral matter	4.08

Summary: First, the comparatively high moisture content is readily explained by the greater relative humidity of this climate; second, the samples examined in this laboratory contain at least 8 per cent of fat.

[8] *Bull. Soc. Chim.*, **39**, 906.

The fat content of a prepared food in which cow's milk is an important ingredient will be subject to considerable variation, but amounts approximating 9 per cent as reported by others are probably too high, due in most cases at least to approximate volumetric methods of estimation; third, the malted milk contains 2.6 per cent of nonnitrogenous organic matter insoluble in hot water which reduces the total soluble carbohydrates from 67.63 per cent (the average of three determinations from different sources) to 65.03 per cent which is in close agreement with our results and which more nearly represents the actual amount of soluble carbohydrates present; fourth, the malted milk in question contains between 16 and 17 per cent of proteids which figures fully substantiate the claims of the manufacturers in this respect; fifth, the product contains about 4 per cent of inorganic salts, which figure is also in close agreement with the average of previous findings.

EDITORIAL.

THE RELATIONSHIP BETWEEN THE EXTERNAL APPEARANCE AND THE ASH CONTENT OF PHILIPPINE COAL.

A quantity of coal from a mine south of Sydney, Australia, was sent to this Bureau in 1907 for test. The coal was fairly compact and for the most part with a hackly fracture. It was markedly characterized by alternating dull and lustrous bands parallel to the bedding planes. The lustrous bands were usually not over a few millimeters in thickness, while the dull layers were many times that. The luster of the lustrous bands was quite brilliant, approaching the vitreous appearance of obsidian. It occurred to me that the difference in the brilliance of the bands might be due to the content of earthy matter. The two were carefully isolated and the ash determined as follows:

Dull portion (per cent).	Lustrous portion (per cent).
12.1	2.6

These numbers show that without doubt a large part of the difference in luster is due to the ash content.

I do not think that coals from entirely different sources are to be compared, but it is quite probable that the luster of coal from the same vein or same field may vary inversely as the content of earthy matter.

I have already called attention[1] to the striking similarity between all the coals thus far discovered in the Philippine Islands, and I have arranged the record of a number of samples of these together with some from Australia in the order of their descreasing ash content, in the following table:

Philippine coals arranged in order of decrease in ash content.

Source of coal.	Ash (per cent).	Luster of the coal.
Tayabas, Mauban	31.50	Very dull.
Negros, near Cadiz	18.00	Dull to sublustrous.
Batan Island	14.70	Dull.
Negros	14.23	Dull to very lustrous, uneven.
Australia	12.55	Dull to lustrous, uneven.
Australia[a]	12.01	Dull.
Australia	9.99	Dull for the most part. Streak very lustrous.
Negros, Escalante	9.55	Sublustrous to lustrous.
Surigao	9.06	Sublustrous, uneven.

[a] Given above.

[1] The Mineral Resources of the Philippine Islands, Bulletin of the Division of Mines, Bureau of Science, Manila, 1908.

Philippine coals arranged in order of decrease in ash content—Continued.

Source of coal.	Ash (per cent).	Luster of the coal.
Philippine Islands	7.86	Sublustrous.
Cebu, near Carmen	7.48	Do.
Philippine Islands	7.22	Sublustrous to lustrous.
Philippine Islands	6.95	Sublustrous.
Cebu, near Carmen	6.50	Sublustrous to lustrous.
Luzon, Rizal	6.20	Lustrous.
Polillo	6.00	Dull to lustrous.
Polillo, Vista de Burdeus	4.38	Sublustrous, uneven.
Cebu, Libing-bato	4.17	Lustrous.
Batan Island, Bett's	4.12	Sublustrous, uneven.
Cebu	3.81	Lustrous.
Zamboanga	3.77	Do.
Tayabas, Antimonan	3.70	Dull to lustrous, uneven.
Samar	3.49	Lustrous.
Cebu, near Carmen	3.28	Do.
Australia[a]	2.60	Very lustrous.
Batan Island, Military Reservation, coal seam No. 5	2.50	Lustrous.
Rock Spring, Wyoming	1.92	Sublustrous.
Mindoro, Bulalacao	1.61	Do.
Cebu, near Carmen	1.61	Lustrous.

[a] Given above.

These lusters of these coals were nearly all determined [2] at the same time, they are therefore comparable and show that to a marked extent they depend on the content of earthy matter.

Perhaps there are also other conclusions which may be drawn from the ash content of a coal. It is generally known that the value of a coal increases with the size and continues until egg size and lump are reached. It is also generally true that the heating power advances in the same manner, but by no means in the same proportion as the above factors. This increase is due, barring physical conditions, mainly to the diminished quantity of ash which may be seen from the following figures of Mr. Somermeier.[3] The sample was thoroughly air-dried and separated by sifting into various sizes and analyzed by the official method as noted below:

Size in fractions of an inch.	Moisture.	Volatile combustible matter.	Fixed carbon.	Ash.
$\frac{1}{80}$ and finer	2.05	35.54	59.66	*2.75*
$\frac{1}{40}$ to $\frac{1}{80}$	1.90	38.05	58.40	*1.65*
$\frac{1}{20}$ to $\frac{1}{40}$	1.70	38.55	58.35	*1.40*
$\frac{1}{10}$ to $\frac{1}{20}$	1.45	38.80	58.55	*1.20*
$\frac{1}{4}$ to $\frac{1}{10}$	1.15	39.05	58.20	*1.60*

[2] *This Journal, Sec. A* (1907), **2**, 50.

[3] *J. Am. Chem. Soc.* (1906), **28**, 1008.

The greater percentage of moisture in the fine coal is probably accounted for by the phenomena of adsorption. The finer the coal the larger the surface exposed and consequently the greater the quantity of water abstracted from the air and held upon its surface.

ALVIN J. COX.

STARCH PRODUCTION IN THE PHILIPPINE ISLANDS.

The cassava plant (*Manihot utilissima* Pohl) is found in all parts of the Philippines. The Tagalog name is *camoting cahoy*. In the northern islands the tubers are extensively used by the natives as a food during times of need, while with the Moros it forms a staple article of diet. As all Philippine varieties of the plant contain considerable quantities of hydrocyanic acid, the tubers are not used as extensively for stock food as they should be, for the natives generally do not understand how to treat the plant so as to remove this poisonous acid. The problem of obtaining a good and cheap stock food is an exceedingly important one in the Philippines. Nothing appears to me so promising as cassava and the cowpea. The two plants should be grown together. The greatest demand which cassava makes on the soil is in nitrogen, which the cowpea supplies. By a suitable combination of the cowpea, rich in nitrogenous substances, the cassava roots, rich in carbohydrates, and coconut oil-cake, rich in fats, it is a simple matter to make up a first-class, well-balanced stock food. All these substances can easily be made available in the Philippines, so there is no necessity for the importation into the Islands of stock food from foreign countries. If the cassava is planted for its starch, or for alcohol manufacture, some other quick-growing legume such as mungo or peanuts, could be planted with it. These crops will not only pay well in themselves and add nitrogen to the soil, but they serve the further purpose of keeping out the weeds until the cassava is able to take care of itself.

With this introduction as to the best methods of handling cassava, it may be stated that in this plant the Philippines has the cheapest source of starch in the world, and there is only one other substance which at the present time seems able to compete with it as a source of alcohol, a product of which there is a large native supply, namely, the molasses residue from the crystallization of cane sugar. The cheapest alcohol manufactured on any large scale to-day comes from this source, being made in Cuba and Brazil and sold for 10 cents a gallon. Until the methods of alcohol manufacture from cellulose substances (sawdust, etc.) are perfected, the Philippines has in great quantity the two cheapest raw products for alcohol manufacture.

There are no reliable data on the right yield of cassava in the Philippines. In Mississippi and Florida, on good ground, 10 tons of roots are

obtained per acre. The record of yields for this plant found in the literature runs from 4 to 200 tons per acre. In the Philippines the plant has never been raised on a large scale, although several companies are now planting it quite extensively. Plants abount a year old, selected at random from the district in the neighborhood of Zamboanga, Mindanao, averaged 25 pounds of roots each, which, planting 1 meter each way, would give a yield of 50 tons per acre. If 10 tons per acre can be obtained in the Southern States of America, with a possible growing period of from eight to nine months, it would seem to be perfectly safe to figure as much for virgin Philippine soils, with a growing period of twelve months. One acre of ground in the United States will produce on an average 40 bushels of corn containing 1,500 pounds of extractable starch. One acre of cassava in the Philippines will produce at least 10 tons of roots containing 5,000 pounds of extractable starch. If the fermentable matter is converted into alcohol, the comparison becomes even more favorable to the cassava, as the roots contain in addition to the starch, about 4 to 6 per cent of fermentable sugar, so that from the crop of 1 acre of this plant, over 400 gallons of 95 per cent alcohol could be manufactured. Alcohol can be made from cassava for about the same price as from corn and its manufacture from this substance costs in Peoria, Illinois, $0.032 gold per gallon. One can easily figure the price at which cassava alcohol can be sold and still leave a profit.

The cost of manufacturing starch from cassava is also essentially the same as from the potato, and it has been described in a paper soon to appear in the Philippine Agricultural Review by Dr. E. B. Copeland and myself. I shall not treat of it here. If a factory for manufacturing starch from the roots is not available, these may be ground up, dried and sifted, the cassava flour resulting having a starch content of 60 to 75 per cent. Some cassava meal, so prepared by pounding up the roots in a rice mortar and sun drying, has been kept in an open bottle in this laboratory for two years and shows no signs of decay. Dr. H. W. Wiley, of the Bureau of Chemistry, United States Department of Agriculture, quotes a price of $1\frac{1}{3}$ cents, gold, per pound for such crude cassava meal. First-class cassava starch will probably average over 3 cents, gold, per pound, and pearl tapioca prepared from it, about one-half cent higher.

Heating, or very thoroughly washing, is necessary in preparing cassava starch products so as thoroughly to eliminate all the hydrocyanic acid. This acid is apparently present, combined with other substances, in the form of a glucoside, as we have many times noted that cassava roots which had stood until there was a slight decay, had a very powerful odor of this acid, while no such odor may be detected in the fresh root; hence I would recommend to agriculturists of these Islands that in feeding to hogs, the roots should be ground up and either washed many times with water, or better boiled with water into a starch paste.

The analyses of Philippine cassava tabulated below, show it to contain about the same percentage of starch as the same plant found in other parts of the world. The following two plants were from a plantation on Basilan Island, the analyses being made by Mr. Reibling:

Item.	I.	II.
Age of plant ---------- months	10	12
Weight of roots ---------- grams	10,872	14,360
Moisture ---------- per cent	54.6	54.7
Dry residue ---------- do	45.4	45.3
Commercially extractable.		
Air-dry starch ---------- per cent	27	26
Ash ---------- do	.81	.95
P_2O_5 ---------- do	.13	.13
HCN ---------- do	.24	.15
Total N as NH_3 ---------- do	.51	.58
K_2O ---------- do	.15	.18

The large increase in weight noted for twelve months as compared to ten months is worthy of attention, as I have been repeatedly told by Filipinos in many different parts of the Islands that if the plants are allowed to grow for from eighteen months to two years, the tubers will then be very large, weighing 80 to 120 pounds per plant.

Five and three-tenths kilos of cassava of unknown age, from Rizal Province, gave by grinding on a nutmeg grater, 1,350 grams air-dry starch (25 per cent) and 600 grams (11.3 per cent) of fibrous residue containing 64 per cent of starch. Experiment demonstrated that by grinding this fibrous residue dry in a mortar, a further 3.5 per cent of the total of starch could be obtained. However, under present-day conditions of cheap land and cheap labor in the Philippines, it is not good business policy to attempt to obtain any high extraction of the starch from the roots, as to extract this last few per cent costs relatively more than to remove the first 20 per cent of starch and the money can be used to better advantage in raising more roots.

One thousand three hundred grams of cassava roots (said to be 2 years old) were rasped on the machine described in the article referred to above, giving 400 grams of air-dry starch (30.77 per cent) or 27 per cent dry weight, and 110 grams of fibrous residue (8.4 per cent). The starch in this residue was 51 per cent.

Four thousand grams of tubers (age unknown) from Batangas Province, gave 1,050 grams of dry starch (26.2 per cent), and 345 grams of fibrous residue (8.5 per cent).

The above percentages are quoted as samples of the yield of starch which may be obtained in a commercial way from Philippine *camoting cahoy*. Other analyses made in this laboratory run from 24 to 30 per

cent of starch and it seems reasonable to assume that 25 per cent of air-dry starch (14 to 18 per cent water) may be commercially extracted from the plant.

Samples of arrowroot (*Maranta arundinacea* Linn.) grown in the Islands contained from 18 to 22 per cent of starch. The plant is raised only as a food for hogs. It seems rather extravagant to feed to hogs one of the highest priced of starches.

Sincamas (*Pachyrhizus bulbosus* Britton) [*P. angulatus*] tubers gave 2.5 to 10 per cent of commercially extractable starch, according to the age of the plant, the lowest yield being obtained from tubers 2½ months old, and the highest from those 12 months old.

Tacca pinnatifida Forst., yielded 22.3 per cent of starch. This plant is rasped very easily and the starch is more easily obtained in a pure state from it than from any plant I have handled. Tacca starch sells for a higher price than the others, being called in the world's market Bermuda arrowroot.

Dioscorea sp. gave 11 per cent of commercially extractable starch with a total starch content of 14.3 per cent. This starch is remarkable for the small size of its granules.

The seeds of *Cycas circinalis* Linn., which are sometimes used as a source of "sago", yielded 31.2 per cent of starch.

The tubers of *Amorphophallus campanulatus* Blume are very large, but from them we were only able to obtain as the highest yield 4.5 per cent of starch. The presence of numerous spicules of calcium oxalate renders the preparation of an edible starch from this plant very difficult.

RAYMOND F. BACON.

ILLUSTRATIONS.

PLATE I.

FIG. 1. Starch from *Manihot utilissima* Pohl.
2. Same in polarized light.
3. Starch from *Tacca pinnatifida* Forst.

PLATE II.

FIG. 4. Starch from *Tacca pinnatifida* Forst, in polarized light.
5. Starch from *Tacca pinnatifida* Forst.
6. Same in polarized light.

PLATE III.

FIG. 7. Starch from *Dioscorea* sp. In polarized light, this starch shows no change.)
8. Starch from *Cycas circinalis* Linn.
9. Same in polarized light.

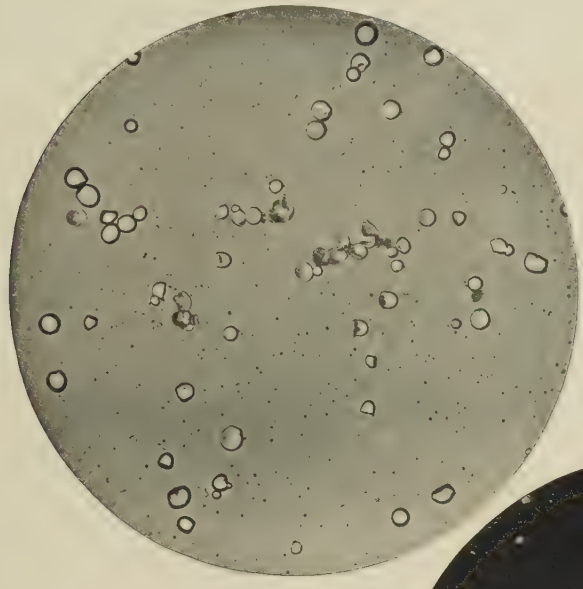

FIG. 1.

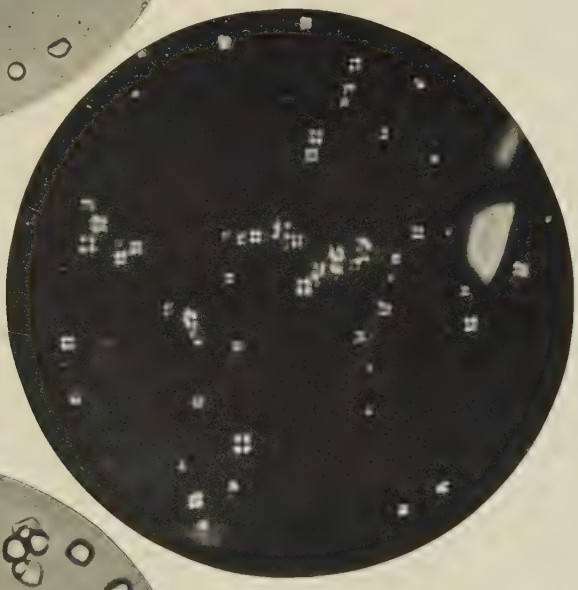

FIG. 2.

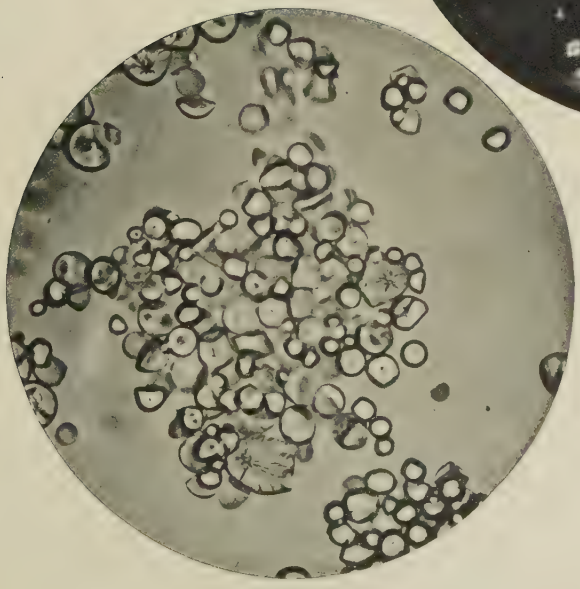

FIG. 3.

PLATE I.

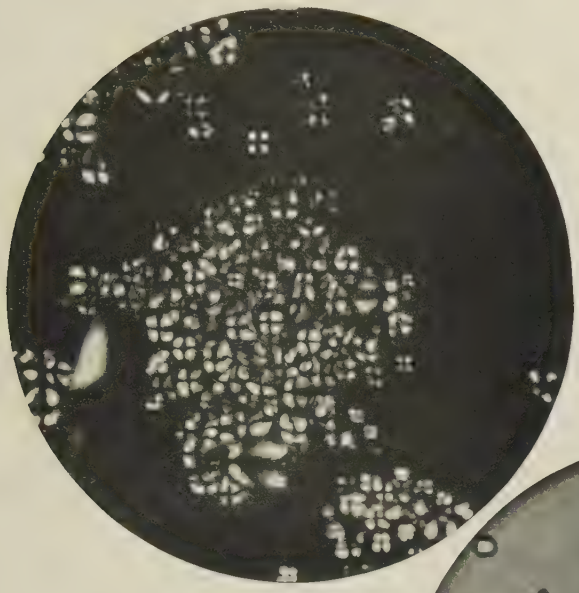

FIG. 4.

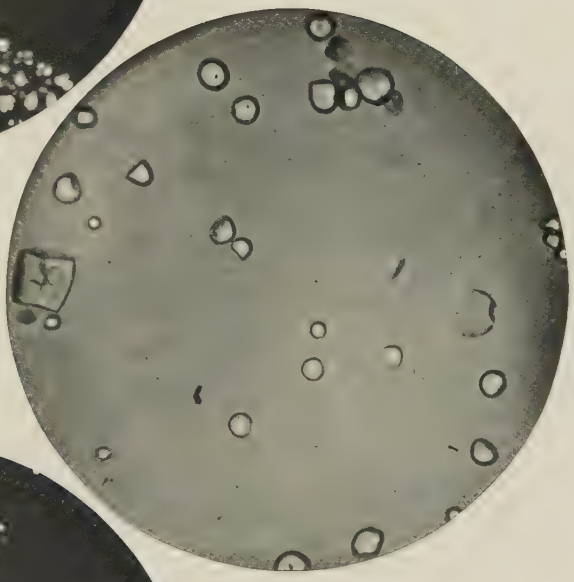

FIG. 5.

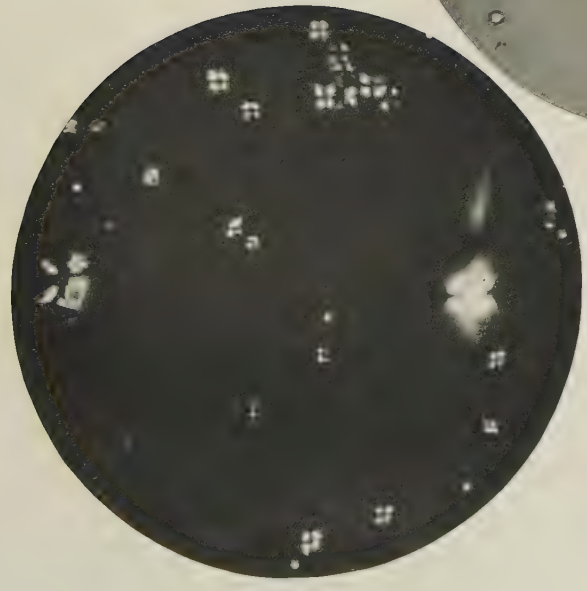

FIG. 6.

PLATE II.

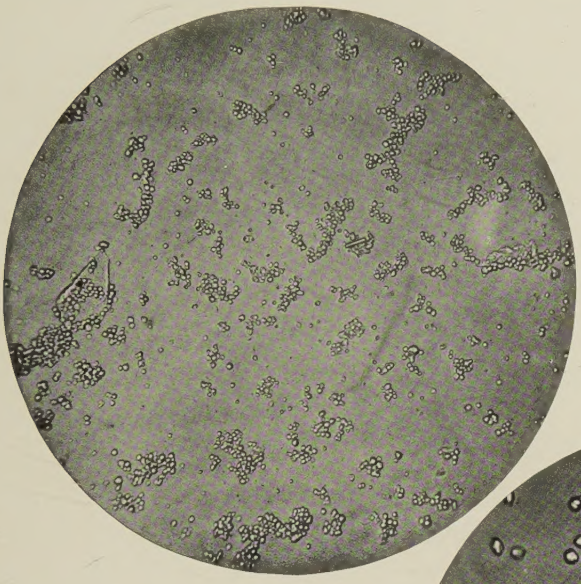

FIG. 7.

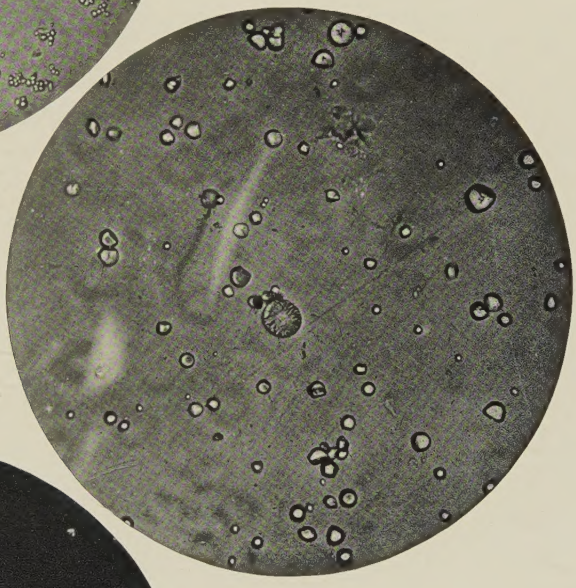

FIG. 8.

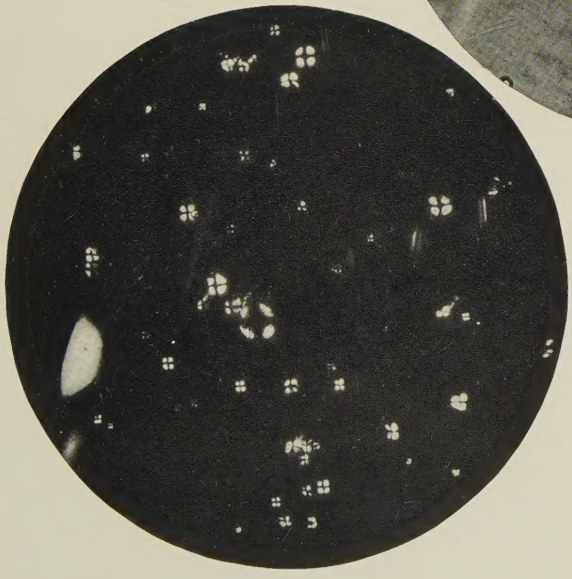

FIG. 9.

PLATE III.

THE ASCENT OF MOUNT PULOG.

The highest mountain in northern Benguet which has ever been ascended so far as is known, is Mount Pulog, recently climbed by Mr. Charles G. Benson and party of the Bureau of Lands. The notes which follow are taken from Mr. Benson's account of the trip.

Mount Pulog is in northeastern Benguet not far from the line between Nueva Vizcaya and Benguet. Kabayan, the settlement from which the start for the mountain was made, is a journey of a day and a half or two days from Baguio. From Kabayan the party went by the regular trail to the barrio of Lutab. One-half mile south of Lutab they turned off on the old Spanish horse trail which runs higher up on the hills than the trail at present used, and followed it to the Adat River. From this point they took a foot trail which runs up the cañon of the river at an average height of about 90 meters above it. After following this for one-half mile they traveled in an irrigation ditch for approximately two miles, then descended to the level of the river, crossing it at a point where two branches, one coming from the south of Mount Pulog and one from the north of that mountain, unite. After crossing the fork from west to east they climbed straight up over a very difficult foot trail to Ankiki, a little Igorot barrio of about four families, at an altitude of approximately 2,190 meters above sea level.

The trail from Ankiki to the top of Mount Pulog runs around the base of the main peak and over the tops of two subsidiary ones, after which it descends to the rancheria of Tinuk or Tinak, which is about 1,520 meters below the top of the mountain and lies to the south of the Asin Grande basin.

The top of Mount Pulog for a distance of about 240 meters below the summit, was found to be covered with very coarse-bladed grass a foot high. The height of the mountain, carefully estimated from barometric readings, is 2,890 meters. Ice five-eighths of an inch thick formed 60 meters below the summit during the night that Mr. Benson and his party spent there. A sufficient quantity of dead pine-wood for camp fires was obtained near the camp, 90 meters below the summit.

The time occupied in travel between the several points on this trip was approximately as follows: Kabayan to Lutab, ninety minutes; Lutab to the first barrio, one hour; the first barrio to the river bed, one and one-half hours; the river bed to Ankiki, four hours; Ankiki to the summit of Mount Pulog, two hours.

The people of the region passed through by this party are Benguet Igorots, but the following differences were noted between them and the main body of the people of the same tribe. The houses at Ankiki, while similar to those of others of this tribe, were rather better built, having sides of boards. The language spoken by the people of this barrio was hardly intelligible to an interpreter who belonged to the Ibaloi division of the Benguet Igorots. The people of Ankiki dress like the other Benguet Igorots. They are called by the latter *Kadasán* which is said to mean the people who live where the oak trees grow. Their only agricultural product is *camotes*. They keep hogs, dogs and a few chickens. They are great hunters and kill large numbers of deer and wild hogs.

The people of the barrio of Tinuk are called *Busols* by the Benguet people. This name is practically meaningless, as it is the common designation for people who seem to the Benguet Igorots more wild and uncivilized than themselves. The people of Tinuk raise rice but do not terrace the hillsides to any considerable extent.

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